On the Electronic Absorption Spectra and the Dipole Moment of the Molecular Compound between Stannic Chloride and Naphthalene

By Hiroshi TSUBOMURA

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Introduction

It has been well known for many years that stannic chloride as well as the halides of various metals, e.g., aluminium, boron, titanium, tin, mercury, etc., can form molecular compounds with organic compounds.[1][2][3] The organic compounds which combine with stannic chloride may be divided into two groups according to whether they contain oxygen or nitrogen atoms or not. Organic compounds of the former group, e.g., ethers, aldehydes, ketones, amines or nitrils, combine with stannic chloride with evolution of heat. On the other hand, for the latter group, composed mainly of aromatic hydrocarbons, it is known that the bond is very weak and in most cases accompanies changes of electronic absorption spectra and dielectric polarizations.

Briegleb and Kambeitz[4] have, by the optical measurements, found that, in a dilute carbon tetrachloride solution, the MC's (molecular compounds) between stannic chloride and aromatic hydrocarbons exist in a 1:1 form. Ulich and his co-workers[5] have measured the molecular polarization of the MC between stannic chloride and benzene, and gave 0.8D for the dipole moment of the MC, assuming that the concentration of the MC is equal to that of the stannic chloride. Strictly speaking, however, this assumption seems to be incorrect.

As for the experimental data concerning the physico-chemical properties of such MC's, not more than those described above have been reported. Also, it seems that no satisfactory theoretical explanation about the nature of the binding forces has yet been made. In an attempt to obtain more experimental knowledge which may be useful for the clarification of these problems, the present author made the following researches on the electronic absorption spectra and dielectric polarizations.

1) Gmelins Handbuch der anorganischen Chemie, 8 Aufl., 1937, Verlag Chemie G.m.b.H., Berlin; J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green. London, 1929.
2) P. Pfeiffer, "Die organische Molekülverbindungen," Ferdinand Enke, Stuttgart, 1927.
3) G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur," Ferdinand Enke, Stuttgart, 1937.
4) Ref. 3, p. 124.
5) H. Ulich, E. Hertel and W. Nespital, *Z. physik. Chem.*, **B17**, 369 (1932).

Experimental

The stannic chloride used was prepared by introducing dry chlorine into a flask which contained fused tin heated to about 350°C. The stannic chloride vapor which was generated in the flask was led, through a cooler, into another vessel. The stannic chloride thus prepared was refluxed with tin for several hours in order to convert the contained chlorine to stannic chloride. The stannic chloride thus obtained is a clear colorless liquid which shows almost an constant b.p. of 113°C. Naphthalene was recrystallised twice from methanol solutions, and dried in a vacuum desiccator containing phosphorus pentoxide for several weeks. (m.p., 80.6°C). Benzene was purified by washing with concentrated sulfuric acid, followed by fractional distillation. Ethyl acetate was dried with calcium chloride and fractionated. (b.p., 76.8°C). Cyclohexane was purified according to the method described by Hinrichsen and Kempf[6].

The measurements of the absorption spectra were made by the Beckman spectrophotometer, model DU. For the measurement of the dielec-

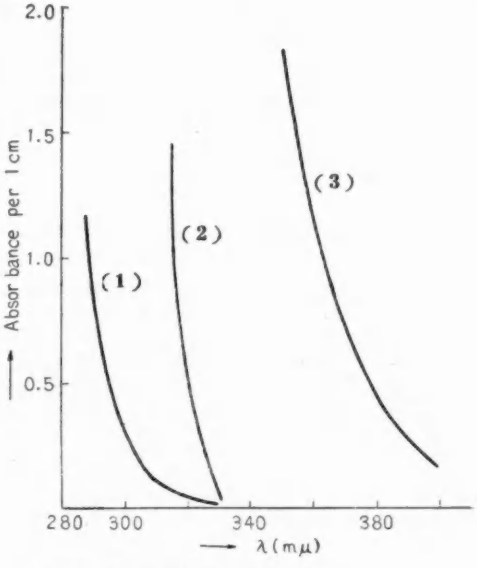

Fig. 1.—Absorption spectra of
(1) pure stannic chloride
(2) 0.0100 M naphthalene in cyclohexane
(3) 0.667 M stannic chloride and 0.0251 M naphthalene in cyclohexane.

6) Hinrichsen and Kempf, *Ber.*, 45, 2106 (1912).

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tric constant, the same instrument as reported by K. Kozima and T. Yoshino[7] has been used in this case. Since stannic chloride is very sensitive to moisture, care was taken to protect it as far as possible during the measurements. As a very small amount of white precipitation was inevitably formed during the preparation of solutions, the solutions were transferred through a glass filter, protected from moisture, into the cells used for the absorption or dielectric measurements.

Results

1. Absorption Spectra—In Fig. 1, curves (1) (2), and (3) show the absorbance per 1 cm of stannic chloride for pure liquid state, that of naphthalene in cyclohexane and that of a mixture of stannic chloride and naphthalene in cyclohexane, respectively. From these curves, it can be seen that, in the region of wavelength longer than 330 mμ, the absorbances of both stannic chloride and naphthalene are negligible, and so the absorbance of (3) in this region is entirely to be attributed to the molecular compound.

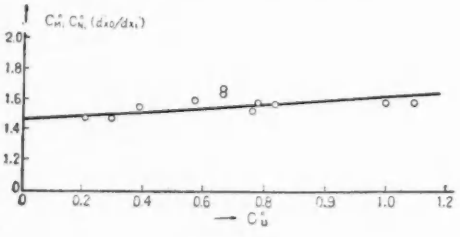

Fig. 2.

Next, the isothermal dilution change of the absorption of this MC was measured for eleven solutions at 18°C. It was confirmed that the results can be expressed by the following equation,

$$c^0_{M\,i}\, c^0_{N\,i}(d_{X0}/d_{Xi}) = (d_{X0}/\varepsilon_X)c^0_{M\,i} + d_{X0}/(\varepsilon_X \cdot K) \quad (1)$$

where $c^0_{M\,i}$ and $c^0_{N\,i}$ are the total concentration (in mole/l.) of stannic chloride and naphthalene (including those which are associated) for the ith solution, d_{X0}/d_{Xi} is the ratio of the absorbance between zeroth and ith solutions which was derived by averaging these ratios at many different wavelengths, and ε_X and K are constants. (See Fig. 2). It may be easily proved that equation (1) can be derived from the following equation expressing the equilibrium of the 1:1 association

$$c_x/c^0_M(c^0_N - c_x) = K^* \quad (2)$$

and in fact K and ε_x appearing in (1) are the equilibrium constant and the molar absorptivity of the MC, respectively. Therefore, the results indicate that in dilute solution the concentration of the MC is governed by equation (2), in agreement with the Briegleb and Kambeitz's results. From the data, K and ε_x were detemined by use of the method of least square. The results are: $K=0.06$ (M^{-1}), $\varepsilon_x = 2\times10^3$($cm^{-1}$. M^{-1}) at 350 mμ. Since in this case K is very small, it seems difficult to get these values more accurately.

TABLE I

at 18°C	x*	d	ε	P_1, cc.	$N_x\Delta P$	N_X, M/gr.	ΔP, cc
$SnCl_4$	0	2.2358	2.9031	45.231	/	/	
Soln. 1	0.01070	2.2198	2.9058	/	0.00093	3.16×10^{-5}	30
Soln. 2	0.03380	2.1897	2.9131	/	0.00303	10.01×10^{-5}	30
at 40°C							
	x*	d	ε	P_1, cc.	$N_x\Delta P$		
$SnCl_4$	0	2.1784	2.8269	45.267	/		
Soln. 1	0.01070	2.1635	2.8245	/	0.00058		
Soln. 2	0.03380	2.1368	2.8307	/	0.00242		

* The x's are the molarities of naphthalene calculated without assuming the formation of the *MC*.

2. Polarization Measurements

The dielectric constants and densities of liquid stannic chloride and two solutions of naphthalene in stannic chloride were measured at 18°C and 40°C. The results obtained are given in Table 1. The dielectric constant and density of stannic chloride itself are in good agreement with those reported by Ulich and others[5]. First, it was found that the polarizations of the solutions were considerably greater than the weighted means of the molecular polarizations of stannic chloride and naphthalene. This indicates that the molecular polarization of the *MC* is larger than the sum of those of stannic chloride and naphthalene.

In a dilute solution, it was confirmed spectrophotometrically that the *MC* was of 1:1 form. But in this case the situation is not quite the same because now naphthalene is dissolved in the liquid of stannic chloride. Nevertheless the author tentatively assumes here that still in this case the *MC* is of 1:1 form, and that the molecular polarization of the *MC*, P_x, is given by the following formula:

$$P_x = P_M + P_N + \Delta P \quad (3)$$

Then the polarization per one gram of the solution is given by

$$P_{12} = (\varepsilon_{12}-1)/(\varepsilon_{12}+2)\cdot d_{12} = N^\circ_M P_M + N^\circ_N P_N + N_x \Delta P, \quad (4)$$

7) K. Kozima and T. Yoshino, *J. Chem. Soc. Japan*, **72**, 20 (1951).

* This is an approximate equation which is exact when c^0_M is far larger than c^0_N. All the solutions investigated were, of course, prepared so as to satisfy this condition.

where N_x is the number of moles (per one gram of the solution) of the *MC* and N°_M and N°_N are those of stannic chloride and naphthalene, including the associated ones, respectively. Concerning P_M and P_N, the former was calculated from the experimental values of ε_M and d_M, and the latter may be taken from the experimental value reported by Briegleb[8], (33.84 cc.). Thus ($N_x \Delta P$) can be determined by use of equation (4). The results obtained are given in Table 1.

The second step is to determine N_x. The concentrations of the *MC* in dilute cyclohexane solutions can be obtained by use of equation (2) with the K value determined from the results of isothermal dilution change. But it is clear that we cannot apply this equation to the solution for the dielectric measurement because the activity coefficient of the medium must differ in the two cases. Therefore the concentration of the *MC* in the solution for the dielectric measurement was estimated by comparing the absorbance of the *MC* in it with that in the dilute cyclohexane solution. The N_x and ΔP thus obtained are given in Table 1.

We may conclude that the orientation polarization constitutes most part of the ΔP. The dipole moment is then calculated from the averaged value of ΔP to be 1.2 *D*. It was found that about 80% of the naphthalene molecules were associated. It is worth while to note that the dipole moment calculated by assuming complete association is 1.0 *D*. This is a little larger than the corresponding value for the *MC* of stannic chloride with benzene reported by Ulich et al.

From Table 1, it can be seen that the $N_x \Delta P$ at 40°C is considerably smaller than that at 18°C. If we assume the dipole moment of the *MC* does not vary with rising temperature, ΔP should be proportional to $1/T$. In such a case we find that the N_x at 40°C is about 60–80% of that at 18°C. From this result, and by use of the *reaction isochore*, the heat of formation is calculated to be 2–4 kcal/mole. But this result should be regarded to be only semi-quantitative, since the agreement between these values for the two solutions was not satisfactory.

The spectra of the MC's of stannic chloride with benzene or ethyl acetate.

From the resemblance of the electronic and molecular structure of benzene and naphthalene, and also from Ulich's polarization data, it was supposed that an absorption spectrum similar to the stannic chloride-naphthalene system would occur in the stannic chloride-benzene system. In order to check this, the spectrum of a stannic chloride solution of benzene has been measured, and the result obtained was in agreement with the expectation mentioned above. (Fig. 3). A quantitative analysis was not made in this case. Simply it was observed that the absorption band of the *MC* was of considerably shorter wavelength than that of the stannic chloride-naphthalene system.

8) G. Briegleb, *Z. physik. Chem.* B **16**, 276 (1932).

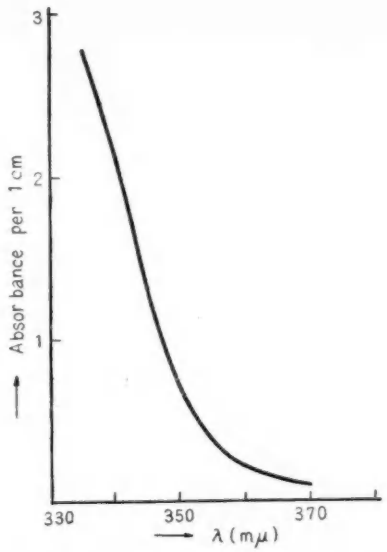

Fig. 3.—Absorption spectra of 0.187 M benzene in stannic chloride.

In an attempt to investigate the spectra of the *MC*'s of stannic chloride with oxygenated organic compounds, ethyl acetate was chosen as an appropriate example. It was observed that much heat was evolved when stannic chloride was dissolved in it. The mixtures are clear viscous liquid and the wavelengths of their spectra are a little longer than that of stannic chloride, but considerably shorter than that of the stannic chloride-naphthalene system. The absorbance of this *MC* was found to be roughly proportional to the concentration of stannic chloride in the mixture. (Fig. 4).

Discussion

It is highly probable that the linkages between stannic chloride and compounds containing oxygen or nitrogen atoms are very strong, since heat is evolved when these substances are mixed. It may be supposed that these linkages are of a type of coördination linkage between the lone pair AO of oxygen or nitrogen atom and the MO of stannic chloride including the d-shell of tin atom.[9] We might explain the linkages between stannic chloride and aromatic hydrocarbons by an analogous model, basing our explanation on the fact that for many cases aromatic hydrocarbons are regarded to be of the electron-donor type. But in this case the orbital of the electron-donor molecule which interacts with that of metal halides is

9) L. Pauling, The nature of the Chemical Bond, Cornell Univ. Press, Ithaca, N.Y., 1940, p. 93.

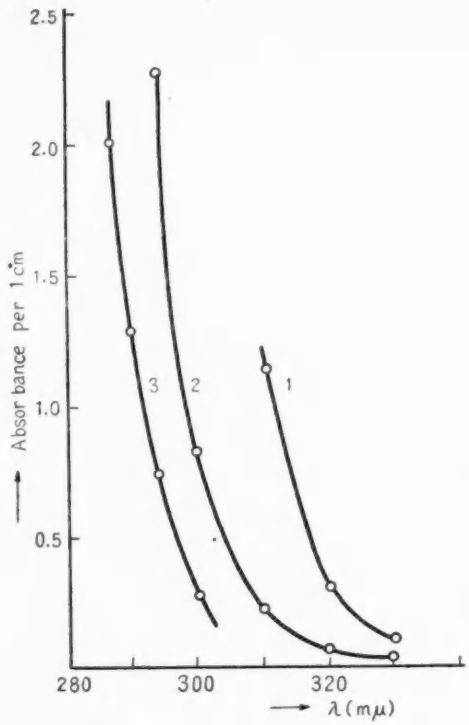

Fig. 4.—Absorption spectra of stannic chloride in ethyl acetate.
(1) 3.57 M stannic chloride
(2) 0.714 M "
(3) 0.202 M "

not confined to one special atom in it, but extends throughout the whole molecule. Then the absorption spectra of such MC's may be understood as the charge-transfer spectra similar to those of the benzene-iodine complex[10] or quinhydrone.[11] If this is true, the dipole moments observed for these MC's may possibly be caused mainly by the charge-transfer.*

Although the energy of the linkage in the MC between stannic chloride and ethyl acetate is very different from those between stannic chloride and aromatic hydrocarbons, it must be concluded that a similar charge-transfer spectrum will exist still in the former MC. The band which was experimentally found to be proportional to the concentration of stannic chloride in the ethyl acetate solution will probably be this charge-transfer spectrum.

From the experimental results, it is likely that the wavelengths of the MC's of stannic chloride become longer as the electron-donors are varied in the sequence of ethyl acetate, benzene, and naphthalene. It is worth while to note that the lowest ionization potentials of the electron-donors become smaller in the same sequence.** The charge-transfer spectra may be roughly assigned to the transition between two energy levels formed by the perturbation between the lowest unfilled MO of the electron-acceptor and the highest filled MO of the electron-donor, and hence the wavelength of this spectrum depends largely on the energy difference between the original unperturbed MO's.[11] Now it is clear that such energy differences become larger, the larger the ionization potentials of the electron-donor. Thus, the relation between the ionization potentials of the electron-donors and the wavelengths of the MC's may be explained by the previously given MO theory.

Summary

The 1:1 form of the molecular compound between stannic chloride and naphthalene in dilute solution has been confirmed by the measurements of electronic absorption spectra. The exaltation of the molecular polarization of this molecular compound has been determined from both optical and dielectric measurements and the dipole moment has been calculated from it. The absorption spectra of other similar molecular compounds have also been measured. It has been proposed that the intermolecular linkages may be explained as the charge-transfer bond.

The author wishes to express sincere thanks to Prof. K. Kozima for his valuable discussions and kind advice.

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10) R.S. Mulliken, *J. Am. Chem. Soc.*, **74** 811 (1952).
11) H. Tsubomura, This Bulletin, **25**, 304 (1953).

* Briegleb took the dipole moment of such *MC*'s as were caused by the deformation of stannic chloride molecule from the tetrahedral structure. (ref. 3, p. 84). It seems that such a cause should also be taken into account as an additive factor of the dipole moment of these *MC*'s. But his explanation for the original nature of the bonds in these *MC*'s seems to be unsuccessful.

** This fact was kindly suggested to the author by Dr. S. Nagakura.

Studies on Santonin. I. Experiments on the Synthesis of Santonin. Part I. Preparation of 2-Keto-1, 10-dimethyl-decalin

By Masanao MATSUI, Seiichi KITAMURA, Yoshio SUZUKI and Michiko HAMURO

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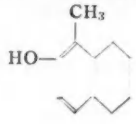
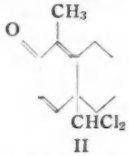
ac-Tetrahydro-1-methyl-2-naphthol (I) is easily obtained from β-naphthol through methylene-dinaphthol and 1-methyl-2-naphthol[1)2)]. T. Harukawa and H. Ishikawa[3)] prepared 2, 5, 6, 7, 8, 10-hexahydro-2-oxo-1-methyl-10-dichloro-methyl-naphthalene (II) from *ac*-tetrahydro-1-methyl-2-naphthol by the method analogous to that of Woodward[4)]. We who aimed from this material to prepare the substance resembling santonin (III), checked



I



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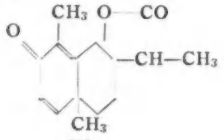

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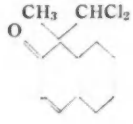
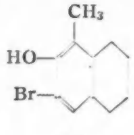


IV

We knew therefore that it is difficult to introduce any radical into the hydrobenzene ring of (II).

Then we turned our attention to the starting material, *ac*-tetrahydro-1-methyl-2-naphthol (II) and tried to introduce a double linkage into its hydrobenzene ring. We treated this naphthol with bromosuccinimide to introduce bromine to the 8-position, but this trial also failed. Considering the fact that the substance obtained by this trial was not dehydrobrominated by alkali in the warm, and showing that bromine exists in the benzene ring and from the results of the bromination of other phenols, replacement of the 3-position of (II) was the most probable. The product obtained was considered to be 1-methyl-3-bromo-tetrahydro-2-naphthol (V), which reacted with chloroform in the presence of sodium hydroxide and yielded dichloromethyl-dienone (VI), mp. 153°.



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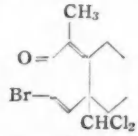
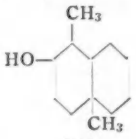


VI

We gave up the first plan and tried to Harukawa's experiment and obtained the reported substance (II) in a lower yield. However, besides this substance we obtained another dienone melting at 63°, probably expressed by the structure (IV).

The substance (II) was so stable that it did not react with bromine and was hardly oxidized by potassium permanganate or phthalmonoper acid.

prepare 2, 3, 4, 5, 6, 10-hexahydro-2-oxo-1, 10-dimethyl-naphthalene (IX) from dichloromethyl dienone (II) above mentioned.



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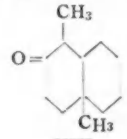

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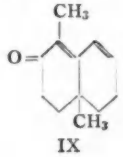

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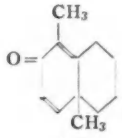

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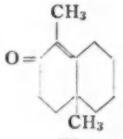


XI

(II) was hydrogenated in an autoclave with Raney Nickel at room temperature. The temperature gradually rose with the consumption of hydrogen and at the end of hydrogenation reached 80°. One mol. of the sample (II) absorbed about 5 mol. of hydrogen and dimethyl-decahydro-naphthol (VII) was obtained. It is a light yellow oil, boiling at 85-100°/0.5 mm. n_D^{18} 1.5075. 3,5-Dinitrobenzoate was oil which was probably the mixture of stereoisomerides. (VII) was oxidized by chromium trioxide in acetic acid and a ketone, bp. 75—85°/0.5 mm. n_D^{18} 1.4955 was obtained. This ketone is 2-oxo-1, 10-dimethyl-decaline (VIII), because its 2,4-dinitrophenyl-hydrazone (mp. 186°) was the same as the

1) K. Fries and E. Hubner, *Ber.* **39**, 439, 441 (1906).
2) Cornforth, Cornforth and Robinson. *J. Chem. Soc.*, **1942**, 682.
3) *J. Pharm. Japan*, **70**, 338 (1950).
4) Woodward, *J. Am. Chem. Soc.*, **62**, 1208 (1940).

one derived from hydrogenation product of 2,3,4,5,6,7,8,10-octahydro-2-oxo-1,10-dimethylnaphthalene (XI) which was prepared from 2-methyl-cyclohexanone and dimethylaminopentanone methiodide by the method of Gunstone and Heggie[5].

Bromination and dehydrobromination by pyridine yielded liquid unsaturated ketone boiling at 65—85°/0.3 mm. n_D^{20} 1.5145—1.5300, 2,4-dinitrophenylhydrazone melting at 189°. This product was probably the mixture of IX, X and XI. (n_D^{20} of IX, X and XI are 1.5590—1.5320 and 1.5260 and 2,4-dinitrophenylhydrazones of IX, X and XI melt at 216°, 238—239° and 198—199° respectively[5].

Experimental

1. *ac*-Tetrahydro-1-methyl-2-naphthol (I)

β-Naphthol condensed with formaldehyde in the presence of sodium acetate in alcohol to give methylene-dinaphthol, mp. 192°, in a theoretical amount. The methylene-dinaphthol was reduced by zinc and sodium hydroxide aqueous solution to 1-methyl-2-naphthol[1], bp. 160–162°/25 mm., mp. 110° (60%). The naphthol was reduced at 110°/100 atm. p. with hydrogen and Raney nickel in alcohol to give *ac*-tetrahydro-1-methyl-2-naphthol, mp. 113° (82%)[2]

2. 2,5,6,7,8,10-Hexahydro-2-oxo-10-dichloromethyl-naphthalene (II)[3]

(I) (70 g.) was dissolved in 700 g. of 10% sodium hydroxide aqueous solution in a 3 l four necked flask. Chloroform (250 g.) and 190 g. of 40% sodium hydroxide aqueous solution were dropped separately but simultaneously from two dropping funnels at 75° during 3 hrs. with stirring which was continued for 45 min. after the addition was over. The cooled mixture was extracted with chloroform (500 cc.) and the extract was washed with 5% sodium hydroxide aqueous solution and then with water. After the evaporation of the solvent, the residue was dissolved in 70 cc. of methanol and the solution was left to stand overnight in a refrigerator. Separated crystals (15 g.) were collected and recrystallized from methanol. 11 g. of (II), mp. 155°, was obtained. (Found: C, 58.70; H, 5.1%; Calcd. for $C_{12}H_{14}OCl_2$ C, 58.8; H, 5.7%.)

The mother liquor of the crystals was distilled, and the fraction boiling at 150–175°/0.25 mm. was collected (35 g.) It was dissolved in methanol (100 cc.) and cooled by dry ice, to give crystals (11 g.), mp. 57–59°. The sample was treated with ether and 3 g. of insoluble crystals (mp. 155°) were obtained. The ether solution, separated from the crystal was washed with 5% sodium hydroxide aqueous solution several times and with water 3 times. Then the ether was removed and the residue was recrystallized from methanol. The substance melting at 63°, a yellowish large prism, was obtained. This is considered to be 1,2,5,6,7,8-hexahydro-2-oxo-1-methyl-1-dichloromethyl-naphthalene (IV). (Found: C, 59.5; H, 5.0; Cl, 28.3% Calcd for $C_{12}H_{14}OCl_2$: C, 58.8; H, 5.7; Cl, 28.7%)

3. *ac*-Tetrahydro-1-methyl-3-bromo-2-naphthol (V)

A mixture of *ac*-tetrahydro-1-methyl-2-naphthol (158 g.), bromosuccinimide (178 g.) and carbon tetrachloride (1 l) was refluxed for 1 hour. After 100 g. of succinimide were recovered by filtration, carbon tetrachloride was removed. The crystals obtained were recrystallized from petroleum ether (bp. 40–60°), giving 78 g. of (V) mp. 71°, (Found: C, 55.06; H, 5.20; Br, 33.5%, Calcd. for $C_{11}H_{11}OBr$: C, 55.2; H, 5.0; Br, 29.2%)

4. 2,5,6,7,8,10-Hexahydro-2-oxo-1-methyl-10-dichloromethyl-3-bromo-naphthalene (VI)

The substance (V) (120 g.), 10% sodium hydroxide aqueous solution (1500 g.) and chloroform (280 g.) were treated in the same manner as case 2. and 12 g. of the desired product (VI) mp. 153°, was obtained. (Found: C, 44.2; H, 4.4%; Calcd. for $C_{12}H_{13}OCl_2Br$: C, 44.4; H, 4.3%)

5. 2-Hydroxy-1,10-dimethyl-decalin (VII)

A solution of 20 g. of (II) in 200 cc. of 5% potassium hydroxide-methanol solution was hydrogenated with 5 g. of Raney nickel catalyst under an initial pressure of 50 atm. p. in 0.5 l. autoclave at first at 20° and at 80° when hydrogenation was over. Twenty hrs. were required and ca. 10 l. of hydrogen was consumed. The hydrogenated solution, after removing the catalyst, was distilled. The fraction boiling at 85–100°/0.3 mm., n_D^{18} 1.5075, which was (VII), was collected. The yield was 16.8 g. (Found: C, 78.2; H, 10.4%; Calcd. for $C_{12}H_{22}O$: C, 79.1; H, 12.1%.) 3,5-Dinitrobenzoate was an oil. Hence the existence of stereoisomerides is probable.

6. 2-Oxo-1,10-dimethyl-decalin (VIII)

In a solution of (VIII) (32 g.) and 500 cc. of acetic acid, 15 g. of chromium trioxide in 120 cc. of water dissolved in 300 cc. of acetic acid was dropped under stirring at 15°. After the addition, when the required 2 hrs., was over, stirring was continued for 3 hrs. and the reaction mixture was left to stand overnight. Water (1.9 l) was added and the mixture was extracted with petroleum ether (bp. 40–60°) five times, using each time 200 cc, of the solvent. The extract was combined and washed with water. 2-Oxo-1,10-dimethyl-decalin (VIII) yellowish oil boiling at 75–85°/0.5 mm., n_D^{18} 1.4955 was obtained, (Gunstone and Heggie reported bp. 76–78°/0.5 mm., n_D^{19} 1.4945)[5]. 2,4-Dinitrophenylhydrazone melting at 186°, recrystallized from methanol, gave no melting point depression on admixture with the sample (186°) prepared by another method[5]. (Found: C, 60.4; H, 7.0%; Calcd. for $C_{18}H_{24}O_4N_4$: C, 60.0; H, 6.7%.)

7. Bromination and Dehydrobromination of (VIII)[5].

Three g. of 2-oxo-1,10-dimethyl-decalin was dissolved in 100 cc. anhydrous ether and 2.8 g of bromine was dropped under stirring and cooled with ice-water. After decolorization, ether was removed and 10 cc. of pyridine was added. The

5) *J. Chem. Soc.*, **1952**, 1441.
6) R.H. Martin and Robert Robinson, *J. Chem. Soc.*, **1943**, 491-7.

mixture was refluxed for 2 hrs. An unsaturated ketone (1.1 g.), bp. 65–85°/0.3 mm., n_D^{20} 1.5145–1.5300, was obtained. 2, 4-Dinitrophenylhydrazone, recrystallized from ethanol, was dark red and melted at 189°.

Summary

2-oxo-1, 10-dimethyl-decalin (VIII) was synthesized from (I), according to the following course, (I)→(II)→(VII)→(VIII). The sample obtained was the same as the one derived from the condensation product of 2-methyl-cyclohexanone and diethylamino-pentanone methiodide.

The writers wish to express their hearty thanks to Dr. Ryo Yamamoto for his stimulating interest in this work, and they are also indebted to Messrs. S. Takai, N. Nishimura, T. Sano and Miss. J. Kigami for the microanalyses.

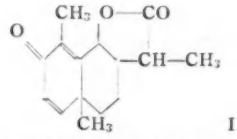
Sumitomo Chem. Co. Ltd, Osaka

Studies on Santonin. II. Experiments on the Synthesis of Santonin. Part II. Preparation of a Stereoisomeride of Santonin

By Masanao MATSUI, Katsuyuki TOKI, Seiichi KITAMURA, Yoshio SUZUKI and Michiko HAMURO

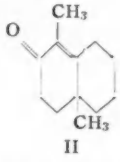
(Received July 22, 1953)

Since the structure (I) had been established for santonin by Clemo, Ruzicka and others[1–5] the synthesis of this compound was unsuccessful, despite of the efforts of several investigators[5,7,8]. Recently Abe, Harukawa, Ishikawa, Miki, Sumi and Toga in Japan[9,10] reported the success of the synthesis of one active and three racemic stereoisomerides of santonin, though the details of the investigations are not published. The present writers have also succeeded independently synthesizing by another route a stereoisomeride of santonin which differs probably from the isomerides obtained by Abe et al.

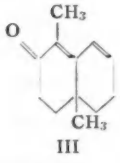


I

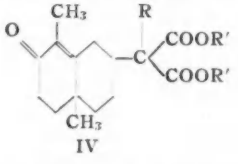
Gunstone and Heggie[11] showed the easy way to obtain 2, 3, 4, 5, 6, 10-hexahydro-2-oxo-1, 10-dimethyl-naphthalene (III) through 2, 3, 4, 5, 6, 7, 8, 10-octahydro-2-keto-1, 10-dimethyl-naphthalene (II) in a moderate yield. The writers found that alkyl malonates condensed with the dienone (III) on the 7-position in the presence of sodium methylate and produced



II



III

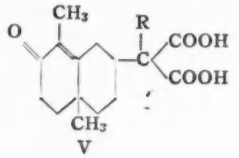


IV

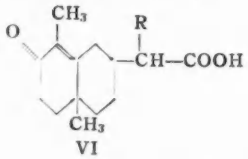
2, 3, 4, 5, 6, 7, 8, 10-octahydro-2-oxo-7-naphthyl-malonates (IV) in a moderate yield. Malonates generally condense with α,β-unsaturated carbonyl system C=C−C=O at the β-position; the condensation is widely known as Michael-condensation. But this condensation never occurs with the enone (II), because probably the β-position (9-position of naphthalene) is highly sterically hindered. On the contrary, malonates easily condense with dienone (III) at the δ-position (7-position of naphthalene). The position was confirmed by selenium-dehydrogenation of the compound obtained by hydrogenation of the condensation product of diethyl methylmalonate and (III) the compound obtained by selenium-dehydrogenation was identified with 1-methyl-7-ethyl-naphthalene by the mixed melting point determination of picrate, mp. 94°.

1) Clemo, Haworth, Walton, *J. Chem. Soc.*, **1929**, 2368; *ibid.* **1930**, 1110.
2) Clemo, Haworth, *ibid.* **1930**, 2579.
3) Ruzicka, Eichenberger, *Helv. Chim. Acta.*, **13**, 1117.
4) Tshitschibabin, Schtschukina, *Ber.* **63**, 2793.
5) Wedekind, Tettweiler, *Ber.* **64**, 387; *ibid.* **64**, 1117.
6) Paranjape, Phalnikar, Bhide, Nargrund, Rasayanam **1**, 233 (1943); *C. A.* **38**, 4266 (1944). (Note: They reported the synthesis of santonin, but none has succeeded to check it.)
7) Gunstone, Heggie, *J. Chem. Soc.*, **1952**, 1354, 1437.
8) Clemo, McQuillin, *ibid.* **1952**, 3835, 3839.
9) *Japan Acad.*, **28**, 425 (1952).
10) *ibid.* **29**, 113 (1953).
11) *J. Chem. Soc.*, **1952**, 1440.

Dicarboxylic acids (V) were obtained by alkaline hydrolysis of esters (IV), and divided into a crystalline substance and a semisolid oil. Acids (V) were changed by decarboxylation to monocarboxylic acids (VI) which were divided into crystal and semisolid oil.



V

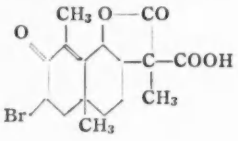


VI

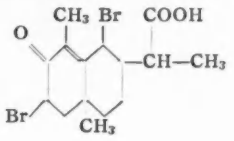
The melting point of (V), (VI) and 2, 4-dinitrophenyl-hydrazone was as follows:—

R	System	V	VI	2, 4-dinitrophenyl-hydrazone
H	A	185°	145°	245°
	B	oil	135°	235°
CH_3	A	183°	125°	235°
	B	oil?	oil?	?

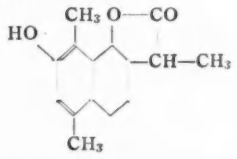
By bromination, crystalline forms of (V) and (VI) ($R=CH_3$) yielded bromolactone-carboxylic acid (VII) (mp. 176°) and dibromo-carboxylic acid (VIII), (mp. 146°) respectively. The constitution of these compounds was proved by analysis and sequent reactions.



VII



VIII



IX

They were dehydrobrominated by heating in an oil bath of about 170° with lutidine (In the case of (VII), decarboxylation also occurred) and produced the same santonin C*, a new isomeride of santonin, melting at 189—190°; λ_{max}^{EtOH} 245 mμ ($\log \varepsilon = 4.10$). The melting point depressed to 138° when santonin C was admixed with an equal amount of natural santonin. The lactone is stable, never colorizes in the sun light, is easily soluble in chloroform and is able to be recrystallized from alcohol, etc. the attitude for various solvents resembling that of natural santonin.

When santonin C was treated with conc. hydrochloric acid, it yielded (±) β-desmotroposantonin (IX), melting at 231°, by dienone-phenol rearrangement, more easily than natural santonin. The desmotropo-santonin was identified by comparing with an authentic sample derived from natural santonin.

Experimental**

1. 2, 3, 4, 5, 6, 7, 8, 10-Octahydro-2-oxo-1, 10-dimethyl-naphthalene (II).[11]

2-Methylcyclohexanone (99 g.), sodamide (18.4 g.) and ether (150 cc.) were stirred for 2–4 hours at room temperature in a three necked flask protected with calcium chloride tube. (A stream of dry nitrogene is not necessary.) 1-Diethylaminopentan-3-one methiodide (135 g.) dissolved in methanol (50 cc.) was added gradually and stirring was continued for 4 hours. The mixture was left to stand overnight. Next day, the mixture was stirred for 2 hours at boiling point. The solution acidified with dil. hydrochloric acid, was extracted with ether. The ether extract was washed with 10% alkali carbonate solution, then with water, was dried, and the ether was distilled out. Octahydro-oxo-naphthalene (II), 45 g. (57%), thus obtained was light yellow oil, bp. 91–92°/0.5 mm. n_D^{29} 1.5217. 2, 4-dinitrophenylhydrazone was recrystallized from ethylacetate-methanol, scarlet plate: mp. 198-199°. (Found: C, 60.3; H, 6.5; N, 15.4%; Calcd. for $C_{18}H_{22}O_4N_4$: C, 60.3; H, 6.2; N, 15.6%.)

2. 2, 3, 4, 5, 6, 10-Hexahydro-2-oxo-1, 10-dimethyl-naphthalene (III).[11]

Dry powder of N-bromosuccinimide (79 g.) was added to a solution of (II) (79 g.) in carbon tetrachloride (200 cc.) and the mixture was refluxed for 30 minutes after the first vigorous reaction ceased. Remaining succinimide was removed from the cold solution. After the removal of the solvent, the residue was refluxed with pyridine (200 cc.) for 2 hours. Hexahydro-oxo-naphthalene (III) (58 g. 73%), bp. 92–96°/0.25 mm., n_D^{18} 1.5562, was obtained. Semicarbazone melted at 210–212° (from alcohol.)

* Since Abe et al. disignated their three isomerides, santonin A. B. and D. The writers named our sample santonin C.

** The melting point reported in this paper is uncorrected.

3. 2,3,4,5,6,7,8,10-Octahydro-2-oxo-1,10 dimethyl-7-naphthyl-malonic acid (V), (R=H).

Diethyl malonate (19 g.) and 10 g. of (III) were added with stirring to a solution of metalic sodium (1.3 g.) in methanol (15 cc.) at room temperature (20°). Stirring was continued for several hours and left to stand for 12–38 hours. The mixture was warmed at 50° with stirring for 2 hours. Acetic acid (5 cc.) was added to the cooled reaction mixture, then water was added, and the mixture was extracted with ether. The ether extract was washed with water and ether was distilled out. The fraction boiling at 160–185°/0.5 mm. (7 g.), which became a semisolid mass, was hydrolysed by refluxing with the solution of potassium hydroxide (7 g.) in aqueous methanol (45 cc.) for 2 hours. The reaction mixture was diluted with water and extracted with ether to remove neutral substances. An oil, alkali soluble, was obtained. It deposited crystals (2.0 g.), which were collected and washed with ether. This crystal is an isomeride of (V) (R=H), mp. 185° (with evolution of CO_2). (Found: C, 64.0; H, 6.8%, Calcd. for $C_{15}H_{20}O_5$: C, 64.3; H, 7.1%.) The mother liquor contains another isomeride of (V), (R=H).

4. 2,3,4,5,6,7,8,10-Octahydro-2-oxo-1, 10-dimethyl-7-naphthyl-acetic acid (R=H).

I) *Acid A*:—The Above mentioned crystalline octahydro-oxo-dimethyl-naphthyl-malonic acid (2.0 g.) was distilled under reduced pressure in an oil bath held at 220°. The whole material distilled at ca. 190°/0.5 mm. and soon crystallized, mp. 144–145° (from ether). (Found: C, 71.2; H, 8.7%; Calcd. for $C_{14}H_{20}O_3$: C, 71.2; H, 8.5%.) 2,4-dinitrophenylhydrazone was scarlet crystal, mp. 244–245° (from acetic acid and methanol). (Found: C, 57.8; H, 5.6; N, 13.5; Calcd. for $C_{20}H_{24}O_6N_4$: C, 57.8; H, 5·8; N, 13.5%).

II) *Acid B*:—Mother liquor of crystalline octahydro-oxo-dimethyl-naphthyl-malonic acid (V) described in 3. was distilled in the same manner as the case of acid A and 2 g. of semisolid mass was obtained. It was dissolved in ether. When the ether solution was concentrated, crystals (1.5 g.) were obtained; mp. 135° (from methanol). (Found: C, 71.5; H, 8.1%; Calcd. for $C_{14}H_{20}O_3$: C, 71.2; H, 8.5%.) 2,4-dinitrophenyl-hydrazone was scarlet crystal, mp. 235° (from acetic acid and methanol) (Found: C, 56.8; H, 6.5; N, 13.2 %; Calcd. for $C_{20}H_{24}O_6N_4$: C, 57.8; H, 5.8; N, 13.5%).

5. α-(2, 3, 4, 5, 6, 7, 8, 10-Octahydro-2-oxo-1, 10-dimethyl-7-naphthyl)-α-methyl-malonic acid (V), (R=CH_3).

Diethyl methylmalonate (20 g.), hexahydro-oxo-naphthalene (III) (10 g.), sodium (1.3 g.) and methanol (15 cc.) were used. The processes were the same as in the case of 3. The product, distilled at 170–190°/0.3 mm., 8.5 g. was hydrolysed by using potassium hydroxide (8 g.) and aqueous methanol (80 cc.) From alkali soluble material obtained, crystals (2.8 g.) melting at 181–183° (when quickly heated, under the evolution of CO_2), recrystallized from methanol, were obtained. The weight of mother liquor was 2.8 g. The crystal is an isomeride of (V), (R=CH_3). (Found: C, 65.8; H, 7.7%; Calcd. for. $C_{15}H_{22}O_5$: C, 65.4; H, 7.5%).

6. α-(2, 3, 4, 5, 6, 7, 8, 10-Octahydro-2-oxo-1, 10-dimethyl-7-naphthyl) propionic acid (VI) (R=CH_3).

(VI) (R=CH_3) was obtained as a crystal mass by decarboxylation which occurred at distillation of crystalline naphthyl-methyl-malonic acid (V) (R=CH_3) (2.8 g.), bp. 180–185°/0.3 mm. The crystal of naphthyl propionic acid (1.9 g.) melted at 125° after recrystallization from ether. (Found: C, 72.3; H, 9.0%; Calcd. for $C_{15}H_{22}O_3$: C, 72.0; H, 8.8%.) 2,4-Dinitrophenylhydrazone was scarlet crystal, mp. 234–235° (from ethyl acetate-methanol) (Found: C, 57.2; H, 6.0; N, 13.1%; Calcd. for $C_{21}H_{26}O_6N_4$: C, 58.7; H, 6.0; N, 13.0%).

Dehydrogenation. Naphthyl-propionic acid mentioned above (1 g.) was hydrogenated in 20 cc. of acetic acid with Adams' platinum oxide (2 mol. of hydrogen was absorbed). The hydrogenated product was treated with selenium (4 g.) at 320° for 18 hours. The neutral product obtained by this treatment was distilled with sodium and converted directly into the picrate, golden yellow needles, mp. 94° (recrystallized from alcohol). Its melting point was underpressed on admixture with 7-ethyl-1-methyl-naphthalene picrate prepared by analogous treatment from natural santonin.

The mother liquor of (V), (R=CH_3) in the case of 5. was also distilled, and semisolid monocarboxylic acid (mixture ?) (2 g., after purification by dissolving in potassium carbonate solution) which did not crystallize, was obtained. 2,4-Dinitrophenylhydrazone were obtained in two forms, one scarlet crystal, melted at ca. 220° and one ca. 195°. The one having higher melting point seems to be that of crystalline acid, mp. 125°, above mentioned, but both of them seem not pure. The semisolid carboxylic acid was also dehydrogenated by selenium after hydrogenation and 7-ethyl-1-methyl-naphthalene picrate, mp. 94°, was also obtained.

7. Santonin C

i) Octahydro-oxo-naphthyl-methyl-malonic acid V (R=CH_3), mp. 183°, (5 g.) was dissolved in 50 cc. of acetic acid under slight heating, and bromine (5.5 g.) dissolved in acetic acid (5 cc.) was added gradually. Bromine was soon decolorized and evolution of HBr occurred. The mixture was poured into 100 cc. of ice water. A crystal (2 g.) separated, was collected and washed with ether. It was bromolactone carboxylic acid (VII) mp. 176°. (Found: C, 50.0; H, 5.3%; Calcd. for $C_{16}H_{21}O_5Br$: C, 51.5; H, 5.6%).

The bromolactone carfoxylic acid (2 g.) and lutidine (10 cc.) were heated at 170° in an oil bath for 2 hours. The mixture was poured into ice water and dil. hydrochloric acid was added. The mixture was extracted with ether and the extract was washed with 10% alkali carbonate solution and then with water. The ether solution was concentrated by evaporation. Crystals separated were collected and recrystallized from ethanol with small amount of active carbon. Rhombic plate (0.4 g.) mp. 189–190°, easily soluble in chloroform, was obtained;

λ_{max}^{EtOH} 245 mμ (log ε=4.10) (Found: C, 73.3; H, 7.2%, Calcd. for $C_{15}H_{18}O_3$: C, 73.2; H, 7.3%). It was stable in sun light and never colorized.

ii) Octahydro-oxo-naphthyl-propionic acid (VI), (R=CH_3), mp. 125° (1.5 g.) was dissolved in chloroform (12 cc.) and bromine (2.0 g.) was added under stirring in the sun light. After decolorization of bromine, dry air was passed through the solution and chloroform was removed together with hydrogen bromide. A small amount of ether was added and crystals (0.8 g) separated were collected and washed with ether. It was (VIII), mp. 145–146°. (Found: C, 44.9; H, 5.3%; Calcd. for $C_{13}H_{20}O_3Br_2$: C, 44.2; H, 4.9%).

The dibromo-compound (0.8 g.) and lutidine (5 cc.) were heated in an oil bath held at 170° for 1 hour and by the same treatment as i), rhombic plate crystal of santonin C, mp. 189–190° (0.1 g.) was obtained.

Santonin C was obtained by the same treatment from crude bromolactone carboxylic acid or dibromocarboxylic acid from which crystals had not been separated.

Mother liquor of naphthyl-methyl-malonic acid and monocarboxylic acid derived from it also yielded santonin C, though the yield was small.

8. Dienone-phenol Rearrangement of Santonin C.

Santonin C (100 mg.) was mixed with 1 cc. of conc. hydrochloric acid. The crystals gradually dissolved and soon different crystals, needles ((±)β-desmotroposantonin) were deposited. The sample, recrystallized from methanol, mp. 231°, which was undepressed on admixture with authentic (±)β desmotroposantonin obtained from natural santonin. (Found: C, 73.5; H, 7.2%; Calcd. for $C_{15}H_{18}O_3$: C, 73.2; H, 7.3%).

Summary

A new isomeride of santonin, santonin C, was synthesized. The route consists of condensation of 2, 3, 4, 5, 6, 10-hexahydro-2-oxo-1, 10-dimethyl-naphthalene and diethyl methylmalonate, hydrolysis, bromination and dehydrobromination by lutidine.

The writers wish to express their grateful acknowledgement to Dr. Ryo Yamamoto for his stimulating interest in this work. They are also indebted to Messrs. S. Takai, N. Nishimura and Miss J. Kigami for the microanalyses and to Messrs. N. Ohi and M. Isaoka for the determination of ultraviolet absorption.

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Emploi du péroxyde d'argent dans le dosage volumétrique et colorimétrique du vanadium[1]

Motoharu TANAKA

(Reçu le 4, Août, 1953)

Introduction

D'études précédentes[2] nous avons conclu que le péroxyde d'argent est un oxydant énergique du manganèse et du chrome. En conséquence nous sommes conduits à lui reconnaître la même propriété dans le dosage volumétrique et colorimétrique du vanadium. Pour cette dernière expérience, on a employé jusqu'à nos jours, le persulfate,[3] l'acide perchlorique,[4] le bromate,[5] et le permanganate.[6] Notre présent travail voudrait ajouter à ces réactifs le péroxyde d'argent.

Dosage Volumétrique du Vanadium

Deux méthodes sont en vigueur pour le dosage volumétrique du vanadium. Dans l'une[7] le gaz sulfureux réduit le vanadium en quadrivalent. Bien que cette méthode aboutisse à d'excellents résultats, elle nous oblige à chasser l'excès de ce gaz par une opération ennuyeuse. Dans l'autre méthode le vanadium est oxydé en quinquivalent par les réactifs mentionnés plus haut.

Il y a longtemps que la séparation éléctrolytique[8] du vanadium d'avec le chrome est faite par l'emploi du cathode de mercure, qui nous donne le vanadium quadrivalent. Cette liqueur éléctrolysée peut être convenablement oxydée par le péroxyde d'argent.

1) Ce rapport a déjà été présenté au "Symposium" de chimie analytique de la Société chimique et de la Société analyticochimique du Japon qui s'est tenu à Tokio, au mois de Mai, 1953.

2) M. Tanaka, This Bulletin **23**, 165 (1950); ibid., **26**, 299 (1953); *J. Chem. Soc. Japan, Section de la chimie pure*, **72**, 29 (1951).

3) R.F. Goddn et D.N. Hume, *Anal. Chem.*, **22**, 1314 (1950); H.H. Willard et P. Young, *Ind. Eng. Chem.*, **20**, 769 (1928).

4) T.D. Parks et E.J. Agazzi, *Anal. Chem.*, **22**, 1179 (1950).

5) I.M. Kolthoff et E.B. Sandell, *Ind. Eng. Chem.*, Anal. Ed., **2**, 140 (1930).

6) B. Bagshave et al., *J. Iron Steel Inst.* (London) **170**, 343 (1952).

7) W. F. Hillebrand et al., Applied Inorganic Analysis, pp. 458-9 (1952).

8) W.F. Hillebrand et al., op. cit., pp. 138-141.

Réactifs Nécessaires

1° Péroxyde d'argent (en suspension dans l'eau distillée).
2° Acide sulfurique.
3° Solution titrée de permanganate de potassium.
4° Solution titrée de sulfate ferreux.
5° Solution d'o-phénanthroline à 0,2%.

Mode Opératoire

1° Absence de chrome et de manganèse.

On dissout dans l'acide sulfurique étendu (1 : 20) un échantillon comprenant 0.5~10 mgr. de vanadium. Après la dissolution complète, on filtre la portion non dissoute. A la liqueur filtrée mélanger de l'eau oxygénée, dont l'excès est subséquemment détruit par ébullition. Refroidir à la température ordinaire et y ajouter du péroxyde d'argent. Chauffer au bain-marie pendant deux minutes. Après disparition de l'oxydant, soumettre à nouveau à la température ordinaire. On y verse alors un excès de sulfate ferreux et 0,5 cc. de solution d'o-phénanthroline. On titre avec le permanganate de potassium jusqu'à la disparition de la teinte rose du complexe fer(II)-phénanthroline. 1 cc de solution centinormale de permanganate correspond à 0,5095 mgr. de vanadium.

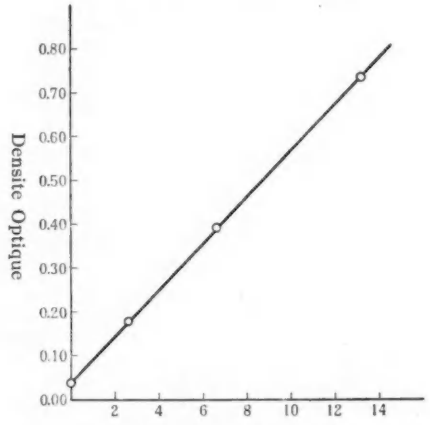
2° Présence de chrome.

Après la dissolution d'un échantillon, on sépare le vanadium d'avec le chrome par l'électrolyse en employant le cathode de mercure. A l'aide du péroxyde d'argent on oxyde ensuite la liqueur électrolysée et on opère suivant le procédé donné plus haut.

3° Présence de manganèse.

S'il existe du manganèse, il est oxydé par le péroxyde d'argent pour former le permanganate. Mais celui-ci est réduit facilement par addition d'une solution de sulfate ferreux jusqu'à disparition de la teinte rose du permanganate.

Fig. 1
Courbe d'étalonnage
Longueur d'onde : 410 mμ
Epaisseur de cuvette : 13,06 mm



Autre procédé pour séparer le manganèse d'avec le vanadium : faire précipiter ce dernier avec le fer ferreux par emploi de bicarbonate de sodium[9], ou encore, par une opération analogue à celle du chrome séparer par l'électrolyse le vanadium d'avec le manganèse, dont il reste cependant des traces dans la solution électrolysée.

Exactitude de la Méthode.

Nous avons répété les titrages sur diverses quantités de vanadium. Ces expériences nous montrent que l'on peut doser la teneur en vanadium avec un écart absolu inférieur à 0,01 mgr. Le tableau I reproduit les résultats.

TABLEAU I

EXACTITUDE DE LA MÉTHODE VOLUMÉTRIQUE

V présent (mg.)	V trouvé (mg.)	Écart absolu (mg.)
0,64	0,66	+0,02
"	0,66	+0,02
"	0,65	+0,01
1,12	1,12	±0
"	1,12	±0
"	1,13	+0,01
1,60	1,60	±0
"	1,59	−0,01
"	1,59	−0,01
3,20	3,20	±0
"	3,20	±0
"	3,21	+0,01
4,80	4,80	±0
"	4,81	+0,01
"	4,81	+0,01

Exemples d'Analyse

Nous donnons ci-dessous les résultats d'analyse des aciers. Pour établir leurs teneurs en vanadium nous avons utilisé la méthode de réduction par gaz sulfureux. Si nous comparons les résultats des deux méthodes, nous sommes frappés par leur coincidence. C'est dire en d'autres termes que le procédé par le péroxyde d'argent que nous avons proposé peut être employé avec succès dans le dosage volumétrique du vanadium.

TABLEAU II

EXEMPLES D'ANALYSE DE LA MÉTHODE VOLUMÉTRIQUE

Échantillons	V trouvé (%)	
	Méthode par le péroxyde d'argent	Méthode employant le gaz sulfureux
Acier	2,52	2,30
"	4,30	4,39
"	4,73	4,72
Ferrovanadium	45,82	45,82
"	45,88	"

9) W.W. Scott, Standard Methods of Chemical Analysis, 5th Ed., p. 1458 (1939).

Dosage Colorimétrique du Vanadium

Pour estimer colorimétriquement la teneur en vanadium on emploie généralement les trois méthodes suivantes;

1°[10] Extraction de l'oxinate de vanadium par l'alcool amylique,

2°[11] Méthode par l'eau oxygénée formant un composé pervanadique,

3°[12] Méthode de E.B. Sandell qui s'appuie sur la coloration du phosphotungstovanadate. Cette dernière est préférée pour deux raisons: peu d'éléments font obstacle au dosage; et par ailleurs la loi de Beer se verifie dans une très grande étendue de la concentration. L'emploi de cette méthode nécessite l'oxydation du vanadium en quinquivalent. Cette oxydation est faite avec succès par le péroxyde d'argent.

Réactifs Nécessaires.

1° Péroxyde d'argent (en suspension dans l'eau distillée).
2° Acide phosphorique, G.P.
3° Acide sulfurique, G.P.
4° Tungstate de sodium à 5 M.
5° Solution d'acide oxalique à environ décinormale.

Mode Opératoire.

A une solution froide (2~3 N d'acide sulfurique) ajouter du péroxyde d'argent et chauffer ensuite au bain-marie pour détruire son excés. Si on y observe une teinte rose due à la présence du manganèse, la décolorer par des gouttes de solution d'acide oxalique. Refroidir à la température ordinaire et diviser la solution en deux parts égales. L'une sera utilisée comme référence. A chaque 10 cc de l'autre, verser 1 cc d'acide phosphorique (1:2) et 0,5 cc de tungstate de sodium. En suite faire bouillir cette dernière solution pendant quelques minutes; comparer la coloration après refroidissement.

Influence des Éléments Étrangers.

Les éléments suivants formant les composés peu solubles sont à écarter[12]:

K, Ammonium, Ti, Zr, Bi, Sb, Sn.

Cependant si on n'observe qu'une petite quantité de précipité, la filtration simple nous amène à un résultat satisfaisant. L'introduction de l'argent ne gêne pas ce dosage. Si le chlorure d'argent se produit, on peut facilement le rendre soluble par addition du sulfate mercurique[13].

Exactitude de la Méthode.

En employant une solution de vanadium quadrivalent de concentration précédemment fixée par la méthode volumétrique, nous avons cherché à établir la relation entre la concentration et la densité optique (longueur d'onde, 410 mμ). La figure 1 nous montre cette relation. Nous avons aussi obtenu l'équation suivante à l'aide de la méthode des moindres carrés:

$$X=\frac{E-0,036}{0,0537}$$

X: concentration du vanadium (microgrames V par cc.)

E: densité optique (épaisseur de cuvette, 13,06 mm.)

Nous avons répété les dosages sur diverses quantités connues du vanadium quadrivalent. A l'aide de l'équation précédente nous arrivons aux résultats du tableau III.

TABLEAU III

EXACTITUDE DE LA MÉTHODE COLORIMÉTRIQUE

V. présent (mg.)	V. trouvé (mg.)	Ecart absolu (mg.)
0,000	<0,0005*	<0,0005*
0,066	0,066	±0
„	0,067	+0,001
„	0,067	+0,001
0,165	0,165	±0
„	0,166	+0,001
„	0,166	+0,001
0,330	0,326	−0,004
„	0,326	−0,004
„	0,323	−0,007

* Résultat de plusieurs expériences répétées.

La conclusion est que par la méthode proposée nous pouvons doser 0,00~0,20 mg. de vanadium avec un écart absolu de ±0,001 mg.

Exemples d'Analyse

Nous donnons di-dessous deux exemples d'analyse par cette méthode:

TABLEAU IV

ÉXEMPLES D'ANALYSE DE LA MÉTHODE COLORIMÉTRIQUE

Échantillons	V. trouvé (%)	
	Méthode par le péroxyde d'argent	Méthode employant le gaz sulfureux
Échantillon composé (Fe 100 mg., Cr 10 mg.	1,52	1,50
Acier au nickel et chrome	0,065	0,064

La coïncidence entre le résultat obtenu par le dosage volumétrique et celui par la colorimétrie est frappante.

Résumé

Nous proposons le péroxyde d'argent comme oxydant dans le dosage du vanadium. Ce réactif peut s'appliquer à la méthode soit volumétrique soit colorimétrique. Quand il existe en même temps diverses substances

10) J. M. Bach et R. A. Trelles, *Sol. obras. sanit. nacion Buenos Aires*, 5, 127 (1941); E. Sudo, *J. Chem. Soc. Japan*, Section de la chimie pure, **72**, 817 (1951).
11) E.R. Wright et Mellon, *Ind. Eng. Chem.*, Anal. Ed., **9**, 375 (1937).
12) E.B. Sandell, Colorimetric Determination of Traces of Metals, pp. 607-9 (1950).
13) M. Tanaka, *J. Chem. Soc. Japan*, Section de la chimie pure, **72**, 136 (1951).

réductrices et le vanadium dont la valence est inconnue, le péroxyde d'argent peut oxyder tout le vanadium en quinquivalent. La puissance de ce réactif sera observée dans le cas suivants:

1° Quand on se sert de la cathode de mercure pour la séparation du vanadium d'avec le fer et le chrome.

2° Quand il existe du vanadium quadrivalent et quinquivalent et que l'on désire évaluer les deux séparément. C'est surtout dans le cas où l'on emploie la résine à ion-échange pour la séparation préliminaire de cet élément.[14]

3° Quand on coprécipite le vanadium avec l'hydroxyde ferreux.

Nous ne voulons pas manquer, en terminant, de remercier cordialement Monsieur le Professeur Sugawara qui nous a encouragé pendant cette recherche et Monsieur le Professeur Hirano qui a mis à notre disposition les échantillons nécéssaires.

Notre étude a été facilitée par le "Coleman's Model 14 Universal Spectrophotometer" donné à la Faculté des Sciences de l'Université de Nagoya par "Elizabeth Thompson Sciencé Fund", à qui nous offrons notre profonde gratitude.

Institut de Chimie, Faculté des Sciences, Université de Nagoya

14) J.E. Salmon et H.R. Tieteze, *J. Chem. Soc.*, **1952**, 2324.

Studies on the Oxy-acid Phosphors. II. Vanadate Phosphors (Part 1)

By Yoshihide KOTERA and Tadao SEKINE

(Received August 19, 1953)

Introduction

Study of the vanadate phosphors was begun by R. Robl[1] who reported the emission of alkali-earth pyrovanadates. A. Schloemer,[2] W. A. Weyl[3] and L. Burns[4] studied the magnesium and zinc vanadates, but the details of their preparations, characteristics, etc. are unknown. We prepared the vanadate phosphors and measured their brightness and emission spectra.

Experiments and Results

Purification of Ammonium Metavanadate and Metallic Salts.

In the preparation of the phosphor, a chemically pure grade of commercial ammonium metavanadate was used as one of the starting materials. The ammonium metavanadate was dissolved in a dilute solution of caustic soda (ca. 5%) until it was saturated. By the addition of recrystallized ammonium chloride to this solution, ammonium metavanadate was crystallized out, and filtered. After this purification procedure was repeated once more, the product was used as one of the batch materials for the dry process. For the wet process, the aqueous solution of this product was used.

Other batch materials were used for the purified metallic carbonate, oxide or hydroxide for the dry process, and for the wet one the aqueous solution of the purified metalic chloride or sulfate. A chemically pure grade of commercial metallic salts was purified as follows. Calcium, strontium or barium chloride was dissolved in water, the impurities due to iron and other heavy metals were removed by the usual chemical methods. This purification procedure was repeated once more, and the filtrate was used for the wet process. The sodium carbonate solution, which was treated in almost the same way as the purification procedure described above, was added to the purified metallic salt solution and the precipitated carbonate thus obtained was used for the dry process. When metallic oxide was needed, the carbonate was heated. The purification of zinc or cadmium sulfate solution was carried out in almost the same way as the procedure described above, except that hydrogen sulfide was passed until a small amount of zinc or cadmium sulfide was precipitated, and that the metallic zinc or cadmium was added to remove the traces of heavy metals which might be present.

As to magnesium salt, magnesium sulfate solution was purified in the same manner. For the dry process, purified basic magnesium carbonate or Merck's unpurified magnesium oxide was employed.

The purity of these batch materials was tested spectroscopically and colorimetrically.

Mixing and Firing

In the wet process, each metallic salt solution was added to the ammonium vanadate solution, and the metallic oxide or carbonate was mixed to the precipitated metallic vanadate in the agate mortar. As for the dry one, crystal of ammonium vanadate was mixed well with the metallic oxide or carbonate in the dry state. The mixed batch was heated at 640°C. for 2 hours.

The firing was done in air in the electric furnace. Three weight percent of ammonium perchlorate was added before firing, because the rise of brightness was expected.[5]

Read before the Third Annual Meeting of the Chemical Society of Japan 1950. Report I was published in the *J. Chem. Soc. Japan Ind. Chem. Sect.*, **54**, 625 (1951). (in Japanese)

1) R. Robl, *Z. Angew. Chem.*, **39**, 608 (1926).

2) A. Schloemer, *J. prakt. Chem.*, **133**, 51 (1932).

3) W.A. Weyl, *U.S. Pat.* 2,322,265; *Ind. Eng. Chem.*, **34**, 1035 (1942).

4) L. Burns, *U.S. Pat.* 2,452, 518.

5) Y. Kotera and T. Sekine, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **54**, 625 (1951). (in Japanese)

TABLE I

THE COLOR OF EMISSION OF PYROVANADATE PHOSPHORS

	3650 Å	2537 Å	cathode-ray or X-ray	previous results
$Ca_2V_2O_7$	no luminescence	blue	no luminescence	red brown (U. V.)[5]*
$Sr_2V_2O_7$	yellowish green	blue	white	yellow (U.V.)[1]
$Ba_2V_2O_7$	bluish green	yellowish green	bluish green	yellow (U.V.)[1]
$Mg_2V_2O_7$	yellow	yellowish brown	orange	—— §
$Zn_2V_2O_7$	yellow	orange	yellow	yellow[3, 4]
$Cd_2V_2O_7$	yellow	orange	yellow	——

*A. Schloemer reported that calcium metavanadate emits the very weak luminescence of wine red color.[2]

§A. Schloemer reported that magnesium metavanadate emits the green luminescence at -180°C.[2]

TABLE II

THE OPTIMUM MIXING RATIO OF PYROVANADATE PHOSPHORS

	Wet process (Metallic vanadate) : (MO or MCO_3)	Dry process (NH_4VO_3) : (MO or MCO_3)
$Ca_2V_2O_7$	10 : 1 (wt., CaO was used)	1 : 1.5 (mol., CaO was used)
$Sr_2V_2O_7$	10 : 1 (wt., $SrCO_3$)	1 : 1.25 (mol., $SrCO_3$)
$Ba_2V_2O_7$	10 : 1 (wt., BaO)	1 : 1.25 (mol., BaO)
$Mg_2V_2O_7$	2.5 : 1 (mol., MgO)	1 : 3.5 (mol., basic Mg carbonate)
$Zn_2V_2O_7$	1 : 1 (mol., ZnO)	1 : 2 (mol., ZnO)
$Cd_2V_2O_7$	1 : 1 (mol., $CdCO_3$)	——

TABLE III

THE RESULTS OF THE CHEMICAL ANALYSIS OF PYROVANADATE PHOSPHORS

	Experimental		Theoretical for $R_2V_2O_7$	
	V_2O_5	RO	V_2O_5	RO
Strontium pyrovanadate	36.4	56.0	46.74	53.26
Barium pyrovanadate	34.1	62.3	37.24	62.76
Zinc pyrovanadate	—	55.0	52.78	47.22

The Properties of Phosphors.

The colors of emissions of the heated products were listed in TAB. I, and the optimum ratios of mixing, when excited by the 2537Å excitation, were shown in TAB. II. It is common that, when oxy-acid phosphors were prepared, the nonstoichiometric compound gives the brightest phosphor by the ultraviolet excitation, and the results obtained might be explained by this rule. Especially, magnesium pyrovanadate showed the brightest value, when prepared with a great excess of magnesium oxide. For the upper three in TAB. II, the precipitates have the form of pyrovanadate ($R_2V_2O_7$), while, for the lower three, metavanadate ($R(VO_3)_2$).[6] The phosphors would be in the pyrovanadate form, and the results of the chemical analysis of some products in TAB. III support this idea. For zinc pyrovanadate, the results in TAB. III were near to the theoretical value for $Zn_3V_2O_8$, which was reported by W. A. Weyl,[3] and contains 57.20% of ZnO, but we consider that the phosphor itself would be in the form of pyrovanadate, in which the excess of ZnO might be present as solid solution.

The emission spectra of some phosphors were shown in Fig. 1, no correction being made on the spectral sensitivity of the photographic plate, and, since their exposure times were not the same, their relative intensity can not be compared strictly. Their spectral range is fairly wide, and this property may be advantageous for practical uses. Further, the emissions of zinc and cadmium pyrovanadates are rather stronger than the others.

As zinc pyrovanadate seemed to be better from the standpoint of application, the preparation of zinc pyrovanadate was studied in detail.

The Preparation of Zinc Pyrovanadate Phosphors.

Both dry and wet processes were tried and the brightness of the samples produced was measured by the apparatus as illustrated in Fig. 2, under the excitation by a low-pressure mercury discharge lamp through the filter Corning No. 7-54, whose spectral transmission is shown in Fig. 3. The reflections from samples were calibrated by measuring the reflection from magnesium oxide, which shows no luminescence. The relative value of

6) J.W. Mellor "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" (1922) Vol. IX p. 768.

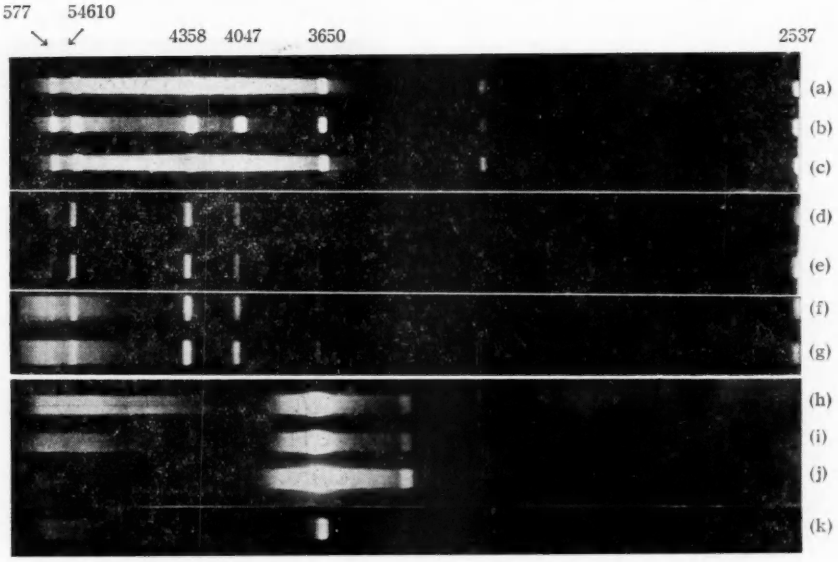


Fig. 1. The emission spectra of vanadate phosphors

(a) $Ca_2V_2O_7$, (b) $Ba_2V_2O_7$, (c) $Ca_2V_2O_7$, (d) $Sr_2V_2O_7$, (e) $Mg_2V_2O_7$, (f) $Zn_2V_2O_7$ (g) $Cd_2V_2O_7$ (h) $Ba_2V_2O_7$ (i) $Sr_2V_2O_7$ (j) $Mg_2V_2O_7$, (k) $Cd_2V_2O_7$

(a)—(g): excited by 2537Å

(h)—(k): excited by 3650Å

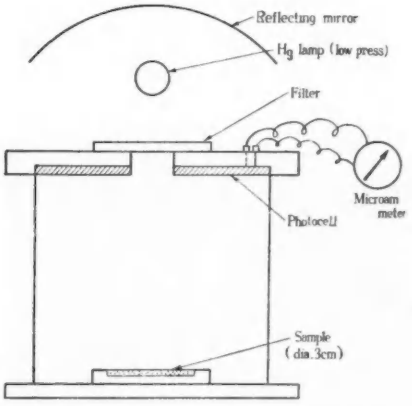


Fig. 2. The apparatus for the measurement of the relative brightness.

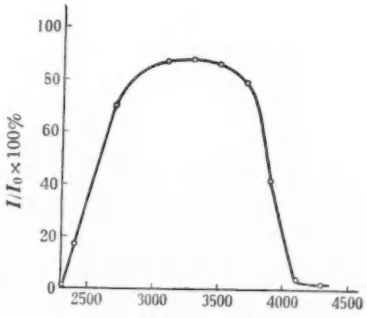


Fig. 3. The spectral transmission curve of the filter, Corning No. 7-54.

brightness was noted, the brightest sample being taken to be 10, while the value of commercial zinc beryllium silicate showed the value 17-20. In the dry process, purified ammonium vanadate and zinc carbonate were mixed well in the agate mortar, 1.2-3 folds of the latter being taken in the molar ratio, and fired 2 hours at 600°C. Results are listed in TAB. IV.

In the wet process, 2 parts of a 5% solution of purified ammonium vanadate were poured into 1 part of a 20% solution of purified zinc sulfate. In some cases alkali was added to the former, and in the other acid was added to the latter, and the effect of *p*H during the precipitation on the brightness of the fired samples was examined. 1 mol. of the precipated zinc metavanadate thus tobained was mixed with 1 mol. of purified zinc

oxide, then fired for 2 hours at 600°C. Results are shown in TAB. V.

TABLE IV

THE BRIGHTNESS OF ZINC PYROVANADATE PHOSPHORS IN DRY PROCESS

The molar ratio	brightness
NH_4VO_3: $ZnCO_3$=1 : 1.2	2
=1 : 1.5	3
=1 : 1.8	9
=1 : 2.0	9
=1 : 2.5	7
=1 : 3.0	6

TABLE V

THE BRIGHTNESS OF ZINC PYROVANADATE PHOSPHORS IN WET PROCESS

pH by the precipitation	brightness
ammonia alkali	9
neutral	10
acidic	9

The effects of adding some heavy metals to phosphors were investigated on the samples obtained by the wet process. Various amounts of heavy metals were added to the precipitate and the mixtures were fired in the same manner as described above. TAB. VI shows the change of

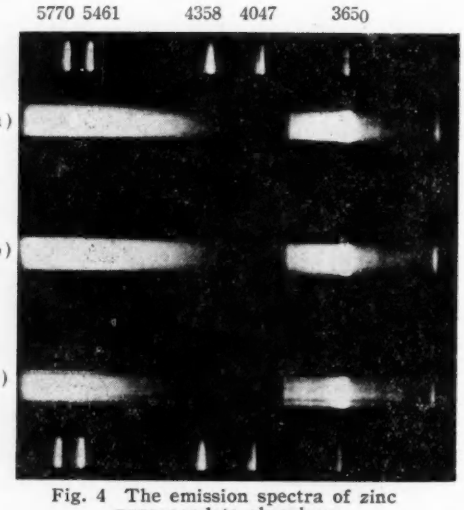


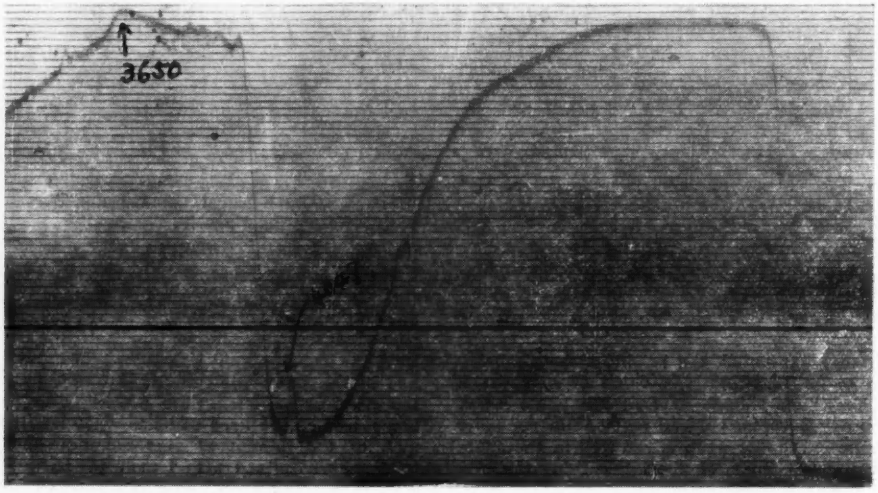
Fig. 4 The emission spectra of zinc pyrovanadate phosphors
Fig. 4—I. The emission spectra.
Fig. 4—II. The microphotometer curve
(a) $Zn_2V_2O_7$ Ag
(b) $Zn_2V_2O_7$ Pb
(c) $Zn_2V_2O_7$ Sn

TABLE VI

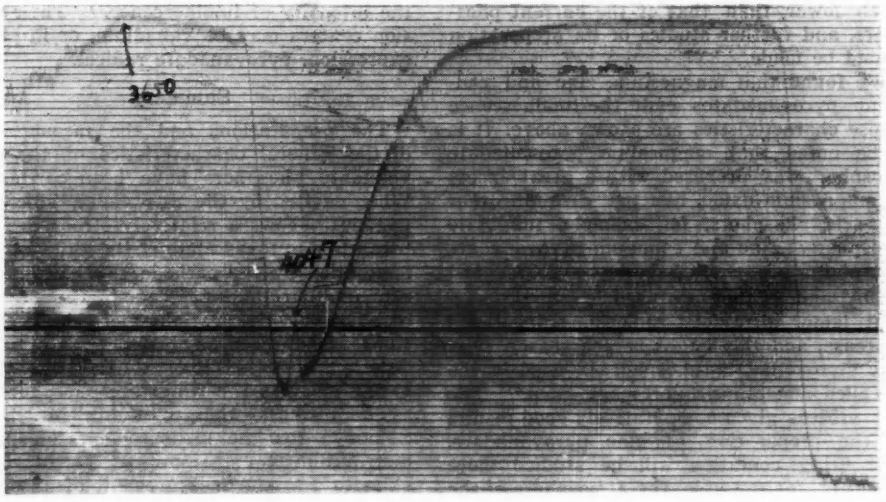
THE EFFECTS OF THE HEAVY METALS ON THE BRIGHTNESS OF ZINC PYROVANADETE

Concentration (mol %) Heavy metals	0.01	0.05	0.1	0.25	0.5	5
Ag	8	10	9	7	7	—
Cu	—	7	—	4	—	—
Pb	10	6	10	8	—	—
Bi	6	4	4	—	7	—
Mn	—	7	—	4	—	—
Sn	8	10	8	8	7	4
Ni	—	7	—	—	—	—
Ce	—	7	—	7	—	—

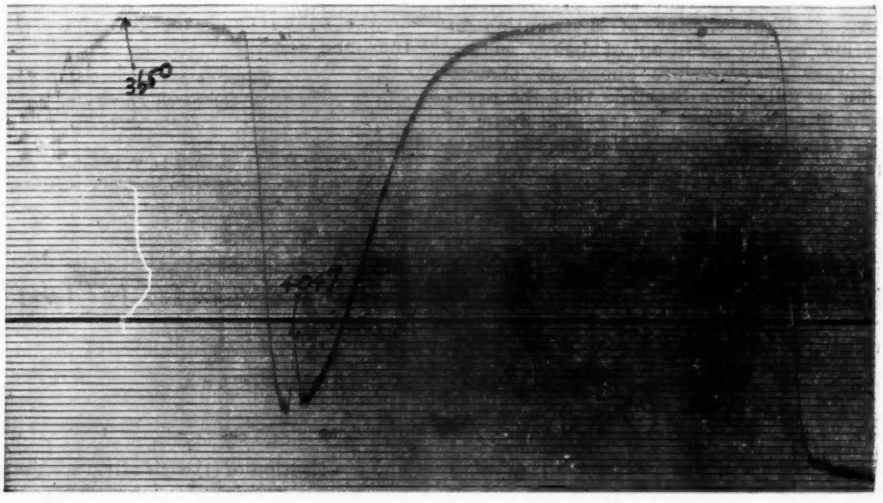
(a) $Zn_3V_2O_7$ Ag



(b) $Zn_2V_3O_7$ Pb



(c) $Zn_3V_2O_7$ Sn



← Deflection of Galvanometer

brightness, when the amounts of heavy metals were changed from 0.01 to 5 mol. % for 1 mol. zinc pyrovanadate. The emission spectra of some samples were shown in Fig. 4, no correction being made on the spectral sensitivity of the photographic plate.

These results indicate that the wet process gives somewhat better results than the wet one in the preparation of zinc pyrovanadate phosphors and the greatest brightness is about a half of that of commercial zinc beryllium silicate, and the heavy metals scarcely change the emission spectra but have the effect of intensifying the brightness.

Discussion

According to Robl, calcium, strontium and barium pyrovanadates show the emission of colors listed in Tab. I. These discrepancies of colors with our results are difficult to explain. As for calcium pyrovanadate, we could recognize its luminescence at 3500–5850Å only by the 2537Å excitation, and could not obtain such a calcium pyrovanadate as emits the red-brown luminescence under any kind of excitation method. Robl found the range of luminescence of strontium pyrovanadate to be 6000–4830Å and that of barium salt 6000–4570Å, while we recognized the luminescence at 4370–5830Å and 3900–5850Å respectively. Strontium pyrovanadate phosphor may be of use for the single white luminescent material

for the Braun tube, but its brightness is much lower than that of the current phosphors, and further studies of its preparation should be made.

We found that magnesium, zinc and cadmium pyrovanadates emit the luminescence whose characteristics are shown above. It is to be noted that magnesium pyrovanadate phosphor was prepared with a great excess of magnesium oxide, like the case of other oxy-acid phosphors, for example, tungstate phosphors. Zinc and cadmium pyrovanadate phosphors are excited both by 2537Å and 3650Å, and, if they are used in the fluorescent lamp, ultraviolet radiation from it will decrease, and this might be the reason why zinc pyrovanadate phosphor is used in the so-called nonactinic fluorescent lamp.[4] The wet process gives comparatively good results in the preparation of zinc pyrovanadate. The firing condition will be studied more precisely, for example, the atmosphere of the firing.

It is ascertained that zinc pyrovanadate shows a slight change of distribution of emission by the addition of heavy metals, and other pyrovanadate phosphors showed similar results. We conclude that the pyrovanadate salts belong to the phosphors of unactivated type similar to the tungstate phosphors. This conclusion is supported by other experiments, for example, by the measurements of the temperature dependence of the intensity of luminescence.[7] Their emission centers may be vanadium, or in precise expression, pyrovanadate radical.

Summary

The preparations and the measurements of the general characteristics of the pyrovanadate phosphors have been carried out. When excited by the ultraviolet, zinc pyrovanadate shows a relatively strong emission. Strontium pyrovanadate emits white color on irradiation by the cathode ray. Magnesium, calcium, barium, and cadmium salts show emission by the various methods of excitation. It has been suggested that pyrovanadate phosphors belong to the unactivated type similar to the tungstate phosphors.

The authors wish to thank Mr. Shigeo Shionoya for the measurements of spectral distribution of emission, Mr. Tetsutaro Hashimoto for the measurement of absorption of filter, and Mr. Hiromi Nishida and Mr. Shoji Makishima for the general discussion on the subject and the experimental work they had done.

Government Chemical Industrial Research Institute, Tokyo
Hatagaya, Tokyo

7) S. Makishima, J. Yamanouchi, T. Mukaibo, S. Shionoya; *Ann. Rep. Eng. Res. Institute*, University of Tokyo, 9, 33 (1951).

On Derivatives of α-Thujaplicin. II. On Nitroderivatives of α-Thujaplicin (o-Isopropyl-tropolone)[1]

By Kameji YAMANE and Shiro MOROSAWA

(Received August 25, 1953)

T. Nozoe and his collaborators[2] previously reported the occurence of hinokitiol and its isomer, α-thujaplicin (I) in the acidic constituents of the essential oil of Thujopsis dolabrata, Sieb. et Zucc. ("Hiba"-wood) produced in Aomori Prefecture in Japan. Again T. Nozoe et al.[3] reported on the derivatives of (I), halogen-, nitroso-, amino-derivatives of (I) and *p*-tolyl-azo-dye, etc. The present authors studied nitro-derivatives of (I) and their rearrangement products.

The authors carried out various mono- and di-nitration of (I) with nitric acid, nitrogen peroxide, cupric nitrate and benzoylnitrate. One kind of mononitro-α-thujaplicin m.p. 112–113° (II) and one kind of dinitro-α-thujaplicin 92–93° (III) are obtained. The separation of (III) from (II) is accomplished by adding aniline or *p*-toluidine to a benzene solution of the mixture of (II) and (III), to precipitate a yellow addition compound of (III). Decomposition of the addition compound with acid gives (III). The cupric nitrate method gives a better yield than any other nitration method: that is, the application of three molar equivalents of cupric nitrate to (I) in acetic acid yields (II) (42%) and (III) (21%), in the case of four molar equivalents of cupric nitrate, it yields (II) (30%) and (III) (24%). But when the mix-

1) This work was presented at the 6th Annual General Meeting of the Chemical Society of Japan in Kyoto, April 2, 1953.

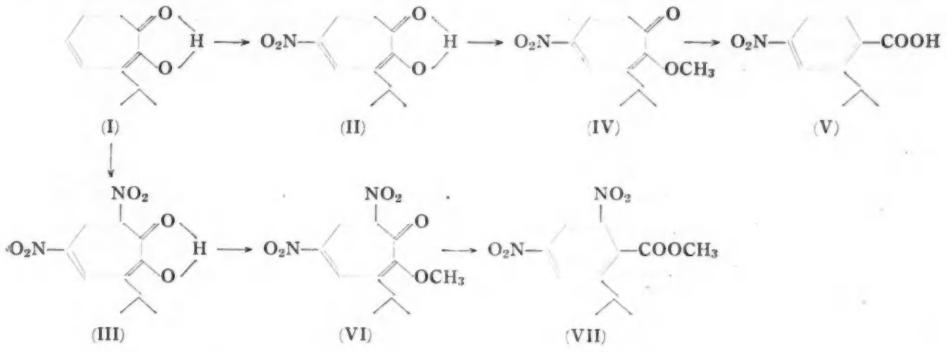
2) T. Nozoe, A. Yasue and K. Yamane, *Proc. Japan Acad.*, **27**, 15 (1951).

3) T. Nozoe, Y. Kitahara K. Yamane, and I. Ikemi, *ibid.*, **27**, 193 (1951).

ture of four molar equivalents of cupric nitrate and (I) in acetic acid is allowed to stand over for five days, (II) (55%) and (III) (14%) are obtained.

The existence of another kind of position isomer of (II) can be considered, but the attempt to find it out during the course of this study was a failure. Moreover, it is noticeable that (II) is unaffected by further nitration with cupric nitrate in an acetic acid solution.

Yellow needles, (II) do not give aniline and *p*-toluidine addition compound but produces a red coloration with ferric chloride. Potassium salt is red prisms, and sodium salt, orange-yellow needles. (II) absorbs three molar equivalents of hydrogen when hydrogenated in methanol with palladium-charcoal as a catalyst, giving amino-α-thujaplicin m.p. 172–173° in a good yield, which is the same substance as that previously obtained by T. Nozoe et al.[3], by the catalytic reduction of the nitroso-deriyative and azo-dye of (I). (II) does not couple with the *p*-tolyl-diazonium compound. From these facts and investigations of the substitution reaction of tropolone, hinokitiol and other tropoloides by T. Nozoe et al.[4], the nitro group in (II) is assumed to be at the *p*-position. Methylation of (II) with diazomethane in ether yields a mononitro-α-thujaplicin methylether m.p. 106.2–106.5° (IV) as yellow prisms in a 92% yield. When heated in methanol with sodium methoxide as a catalyst, (IV) undergoes the rearrangement to yield colorless needles m.p. 143–145° (V) in 86% yield, which is assumed to be a mononitro-*o*-cumic acid from the analytical value, the aromatization of other tropoloides and no coloration by ferric chloride characteristic to tropolone nucleus. The determination of the structure of (V) will be reported on the following paper. (V) gives anilide of m.p. 156–156.5°, and *p*-toluidide of m.p. 189°.



(III) forms yellow prisms m.p. 92–93°, which give a red coloration by ferric chloride characteristic to tropolone nucleus. (III) is soluble in 2N-potassium hydroxide and sodium hydroxide to give a red coloration, but it soon changes to yellow. (III) does not undergo any rearrangement when heated with alcohol, as dinitrohinokitiol[5] does. With aniline, (III) gives an addition compound of orange-yellow needles m.p. 120–122° (decomp.), which are slightly soluble in benzene. With *p*-toluidine, (III) gives also an addition compound of yellow needles m.p. 152–153° (decomp.), but it changes to orange-red crystals of m.p. 161–162° (decomp.) when left for a long time. *o*-Phenylendiamine addition compound forms yellow needles m.p. 155–156° (decomp.), and phenylhydrazine also gives an addition compound m.p. 104–106° in cold benzene, but does not give phenylhydrazone.

Methylation of (III) with diazomethane in an ethereal solution yields a dinitro-α-thujaplicin methylether m.p. 101–102° (VI) as faintly yellow prisms or needles. (VI) undergoes the rearrangement when heated in methanol with sodium methoxide as a catalyst to yield colorless needles m.p. 97–98° (VII) in a 61% yield, which do not show any coloration with ferric chloride. A trial to obtain the free acid by hydrolysis with 2N-sodium hydroxide without isolating the rearrangement product of (VI) gives colorless prisms m.p. 158–160°, which are assumed to be a mononitro-monohydroxy-*o*-cumic acid from the analytical value, but no detailed studies are made. From the investigations of substitution products of tropolone, hinokitiol and other tropoloides by T. Nozoe et al.[4,5], the nitro groups in (III) are assumed to be at the *o'*- and *p*-position. The determination of the structure of (VII) will be reported later.

Ultraviolet absorption spectra of nitro derivatives of (I) and their rearrangement products are shown in Fig. 1 and 2. (II), (III)

and (IV) have absorption maxima of 350–450 mμ characteristic to tropolone nucleus, while (V) and (VII) have not. It is noticeable that (VI) has also no maximum of 350–450 mμ.

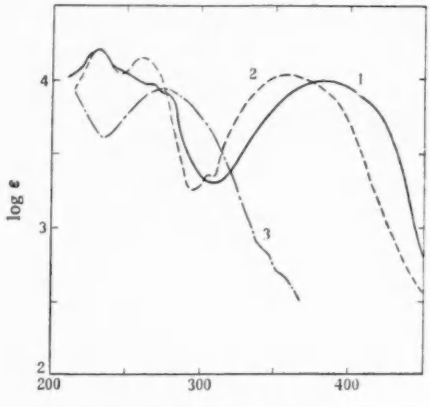


Fig. 1.—Ultraviolet spectra of mononitro-α-thujaplicin (II), (curve 1), mononitro-α-thujaplicin methyl ether (IV), (curve 2), mononitro-o-cumic acid (V), (curve 3) in methanol.

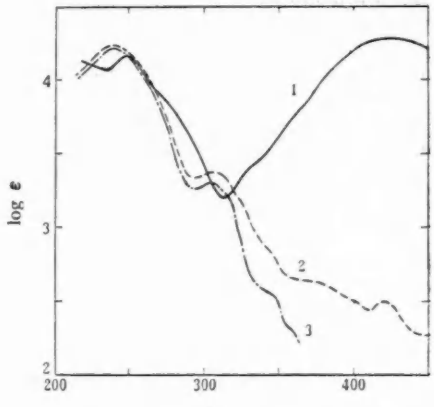


Fig. 2.—Ultraviolet spectra of dinitro-α-thujaplicin (III), (curve 1), dinitro-α-thujaplicin methyl ether (VI), curve 2), dinitro-o-cumic acid methyl ester (VII), curve 3) in methanol.

Experimental

Nitration of α-Thujaplicin (I).

(a) **With Nitric Acid.** 1). To a solution of 1.18 g. of α-thujaplicin (I) in 2 cc. of glacial acetic acid, 0.67g. of sp. gr. 1.42 (68%) nitric acid is added dropwise. The first drop is added at the room temperature, but the subsequent addition is made under ice-cooling during 20 minutes. After the completion of the addition, the mixture is stirred for an hour under ice-cooling, and 0.32g. of yellow crystal of m.p. 105–109° are gained. The recrystallization from benzene gives yellow prisms m.p. 112–113° (II), which give a red coloration with ferric chloride characteristic to tropolones but do not give a *p*-toluidine compound. Yield 20%. Found: C, 57.12; H, 4.82; N, 7.22, Calculated for $C_{10}H_{11}O_4N$: C, 57.41; H, 5.30; N, 6.69%. 2). To a solution of 1.06g. of (I) in 1 cc. of glacial acetic acid, 1.49 g. of sp. gr. 1.42 (68%) nitric acid is added dropwise. The first drop is added at the room temperature, but the subsequent addition is made under ice-cooling during 33 minutes. Yellow crystals begin to separate out after about 10 minutes from the beginning of dropping. After the completion of the addition, the mixture is stirred for an hour under ice-cooling, then the precipitate containing crystals is filtered, and dissolved in benzene and removed from the syrupy matter by decantation. 0.18 g. of (II) are obtained from the benzene solution. Yield 13%. To the filtrate of the precipitation 30 cc. of water is added and the mixture is extracted with benzene. The benzene solution is evaporated to a smaller volume, and aniline is added. Yield, 0.18 g. of an aniline addition compound of (III). Yield of (III), 6%. The recrystallization from benzene gives orange-yellow needles m.p. 118–120° (decomp.). Found: C, 55.38; H, 4.36; N, 11.96, Calculated for $C_{15}H_{13}O_5N_3$; C, 55.48; H, 4.67; N, 12.12%. The decomposition of the addition compound with acid yields (III). The recrystallization from benzene and petroleum ether gives yellow prisms m.p. 92.5–93° (III). Found: C, 47.49; H, 4.04; N, 11.12, Calculated for $C_{10}H_{10}O_5N_2$: C, 47.24; H, 3.96; N, 11.02%.

(b) **With Cupric Nitrate.** To a solution of 2.32 g. of cupric nitrate, $Cu(NO_3)_2 \cdot 3H_2O$, in 5 cc. of glacial acetic acid, a solution of 0.53 g. of (I) in 3 cc. of glacial acetic acid is added dropwise under ice-water-cooling with stirring, and the mixture is left over night in ice-water. To the mixture 25 cc. of water is added, and on standing for an hour, the cupric complex is precipitated. 0.63 g. of the cupric complex is obtained by the filtration, which is decomposed with hot 6N-hydrochloric acid, and extracted with benzene. The benzene solution is evaporated to a smaller volume, and *p*-toluidine is added, yielding an addition compound of (III.) The recrystallization from benzene gives yellow needles m.p. 152–153° (decomp.). Found: N, 12.21, Calculated for $C_{17}H_{19}O_5N_3$: N, 11.63%. The addition compound of *p*-toluidine changes to orange-red prisms m.p. 161–162° (decomp.) when left for a long time, and (III) is obtained from both by the decomposition with acid. 0.17 g. of (III) is gained. Yield 21%. From the filtrate of the *p*-toluidine addition compound of (III), 0.28 g. of (II) is gained. Yield 42%.

Amino-α-thujaplicin. A solution of 0.14 g. of (II) in 25 cc. of methanol is catalytically reduced

4) T. Nozoe, *Science of Drugs*, **3**, 174 (1949); *Sci. Rep. of Tohoku Univ.*, (I), **34**, 199 (1950); T. Nozoe et al., *Proc. Japan Acad.*, **26**, 25, 33, 45 (1950); *ibid.*, **27**, 156, 190, 231, 565 (1951); *ibid.*, **28**, 483 (1952).

5) T. Nozoe, Y. Kitahara, K. Yamane and K. Yamaki, *Proc. Japan Acad.*, **28**, 14 (1950).

with 20 mg. of 5% palladium-charcoal at ordinary temperature and pressure, by which 44 cc. of hydrogen is absorbed. The removal of the catalyst followed by the distillation of methanol gives 0.17 g. of the residue. The recrystallization from benzene and petroleum ether gives yellow prisms, m.p. 172–173°, which do not show any depression of the melting point when fused with amino-α-thujaplicin obtained previously[3] by the catalytic reduction from nitroso-α-thujaplicin and *p*-tolyl-azo dye of (I).

Mononitro-α-thujaplicin Methyl Ether (IV). To a solution of 0.14 g. of (II) dissolved in a mixture of absolute methanol 5 cc. and absolute ether 10 cc., an etherial solution of diazomethane is added under ice-cooling until the mixture no longer gives a coloration with ferric chloride. The removal of the solvent gives 0.6 g. of crystal m.p. 87–99° by standing over in a vaccum desiccator. Yield 92%. The recrystallization from ether gives yellow prisms (IV) m.p. 105–106°. Found: C, 58.75; H, 5.66; N, 6.12, Calculated for $C_{11}H_{13}O_4N$: C, 59.18; H, 5.87; N, 6.77%.

Rearrangement of Mononitro-α-thujaplicin Methyl Ether (IV). A mixture of 70 mg. of (IV) in a methanolic solution of sodium methoxide, prepared from 20 mg. of sodium and 1.5 cc. of methanol, is refluxed for six hours. To this mixture is added 1 cc. of 2N-hydrochloric acid and the mixture is heated in a water bath for an hour, cooled and filtered. 60 mg. of colorless crystals m.p. 140.5–142.5° are obtained. The recrystallization from 50% alcohol gives colorless needles, m.p. 143–145° (V), which are assumed to be a mononitro-*o*-cumic acid, and does not show any coloration with ferric chloride. Yield 86%. Found: C, 57.86; H, 4.86; N, 6.57, Calculated for $C_{10}H_{11}O_4N$: C, 57.41; H, 5.30; N, 6.69%. Anilide of (V) forms colorless prisms m.p. 156–156.5° (from alcohol). Found: N, 9.99, Calculated for $C_{16}H_{16}O_3N_2$: N, 9.86%. *p*-Toluidide of (V) forms colorless needles m.p. 189°. Found: N, 9.40, Calculated for $C_{17}H_{18}O_3N_2$: N, 9.40%.

Addition Compounds of Dinitro-α-thujaplicin (III). Aniline and *p*-toluidine compounds are described above. *o*-Phenylendiamine addition compound forms orange-yellow fine needles, m.p. 155–156° (decomp.) (from alcohol). Found: C, 53.87; H, 4.94; N, 15.00, Calculated for $C_{16}H_{18}O_6N_4$: C, 53.03; H, 5.01; N, 15.41%. Phenylhydrazine addition compound is an orange yellow crystal m.p. 104–106° (decomp.).

Dinitro-α-thujaplicin Methyl Ether (VI). To a solution of 0.13 g. of (III) dissolved in a mixture of absolute methanol 2.4 cc. and absolute ether 7.2 cc., an etherial solution of diazomethane is added under ice-cooling until the mixture no longer gives a coloration with ferric chloride. The removal of the solvent gives 0.087 g. of crystal of (IV) by standing over in a vaccum desiccator. Yield 61%. The recrystallization from methanol gives pale yellow prisms or needles m.p. 99–100° (IV). Found: C, 48.78; H, 4.05; N, 10.17, Calculated for $C_{11}H_{12}O_6N_2$: C, 49.23; H, 4.51; N, 10.45%.

Rearrangement of Dinitro-α-thujaplicin Methyl Ether (VI). (a) A mixture of 48 mg. of (VI) in methanolic solution of sodium methoxide, prepared from 5 mg. of sodium and 1.5 cc. of methanol, is refluxed for six hours. The removal of the solvent gives 36 mg. of colorless scaly crystal m.p. 97–98° (VII). Yield 74%. This crystal is assumed to be a dinitro-*o*-cumic acid methyl ester (VII). Found: C, 49.51; H, 4.55; N, 10.29, Calculated for $C_{11}H_{12}O_6N_2$: C, 49.23; H, 4.51; N, 10.45%. (b) A mixture of 82 mg. of (VI) in a methanolic solution of sodium methoxide, prepared from 5 mg. of sodium and 1.5 cc. of methanol, is refluxed for six hours. After the removal of the solvent, 2 cc. of 2N-sodium hydroxide is added and warmed for two hours in a water bath to effect the hydrolysis. The acidification of the solution with 2N-hydrochloric acid, yields 60 mg. of colorless crystals m.p. 139–150°. The recrystallization from benzene gives colorless prisms m.p. 158–160.5°, which are assumed to be probably a mononitro-monohydroxy-*o*-cumic acid from the analytical value. Found: C, 52.44; H, 4.67; N, 6.79, Calculated for $C_{10}H_{11}O_5N$: C, 53.31; H, 4.92; N, 6.22%.

The authors take this opportunity to express their deep gratitude to Professor T. Nozoe (Tōhoku Univ.) and Professor A. Yokoo (Okayama Univ.) who have given kind guidance during the course of this study. The authors also express their deep gratitude to Takasago Chemical Industries Co. Ltd., for the donation of the essential oil of Hiba-wood, and to the Ministry of Education for their Grant in Aid for Scientific Research.

Department of Chemistry, Faculty of Science, Okayama University, Okayama

Photoconductivity of the Condensed Polynuclear Aromatic Compounds

Hiroo INOKUCHI

(Received August 29, 1953)

Introduction

In previous works, H. Akamatu and the present author have reported that violanthrone, isoviolanthrone and pyranthrone have photoconductivity and intrinsic semi-conductive characters.[1,2] Similar behaviour was found for the other related compounds, that is, the condensed polynuclear aromatic and aza-aromatic compounds.[3,4] For example, indanthrone black ($C_{34}H_{14}N_2O_2$) has the electrical resistivity of $2.5\times10^{8}\,\Omega$cm. and ovalene ($C_{32}H_{14}$) has $2.3\times10^{15}\,\Omega$cm. Such particular pure compounds as these have never been found as shown in Fig. 1 in measurings of the electrical conductivity of many sorts of compounds. And also, this group of compounds shows luminescent character by the actions of cathode-ray and ultra-violet light in the solid state.[5] These characters will be attributed to the intermolecular overlappings of the electron clouds of π-electrons in the polynuclear condensed aromatic rings.

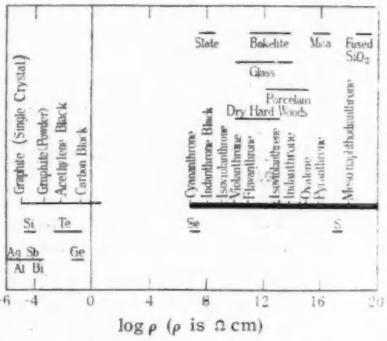


Fig. 1. The electrical resistivity diagram of substances.

Up to the present, the researches of semiconductors have been mostly restricted to the field of inorganic substances, thus these compounds occupy a new field in the branch of semi-conductive materials. We may call these organic compounds—*organic semi-conductors.*

Experimental Procedure

In these compounds, the photoconductivity of isoviolanthrone, violanthrone, isoviolanthrene, violanthrene, pyranthrone, pyranthrene, ovalene, flavanthrone, indanthrone and indanthrazine was measured. These materials have been purified chemically by the usual methods, and then sublimed *in vacuo* more than twice until the electrical conducitvity became constant[3)4)6)].

Excepts for violanthrone and isoviolanthrone, a photocell was made following the so-called "sandwich" type as illustrated in Fig. 2. The cells were formed by evaporating organic semi-conductors (1)* on a quartz plate (dimension is 1 mm × 10 mm × 50 mm) (2) which had been previously coated with a transparent aluminum conducting film (3). The second electrode (4) could be made by depositing a thin layer of aluminum by evaporation on the surface of the film of the organic substances. Further, both sides of this plate were painted with colloidal graphite (5), (6) as electrical terminals. Further details are shown in Fig. 2.

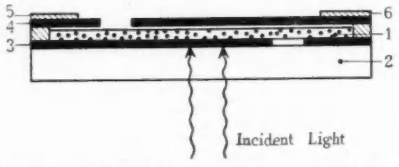


Fig. 2. "Sandwich" type photocell for photoconductivity measurements. (1) photoconductive organic semi-conductor, (2) quartz plate, (3) transparent aluminum electrical conducting film, (4) thin layer of aluminum as a second electrode, (5) & (6) colloidal graphite electrodes as electrical terminals.

For violanthrone and isoviolanthrone, the film of these compounds was deposited by vacuum evaporation between tin foils, 10 mm in width, which were stuck on a quartz plate, keeping the gap between them 1 mm.

The photoelectric current of the cells was produced by illumination of monochromatized light

1) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **20**, 1481 (1952).
2) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).
3) H. Inokuchi, This Bulletin, **24**, 222 (1951).
4) H. Inokuchi, This Bulletin, **25**, 28 (1952).
5) H. Akamatu, unpublished.
6) H. Akamatu and K. Nagamatsu, *J. Colloid Sci.*, **2**, 593 (1948).
* For example, violanthrene are sublimed, at 300°—250°, at 10^{-4} mm.Hg and pyranthrene, at 250°—300°, at 10^{-4} mm.Hg. Heats of sublimation of those are 52.3+2.1 kcal. mol. and 45.3+1.6 kcal. mol. respectively. Details of this problem were reported in this Bulletin, **25**, 249 (1952). H. Inokuchi, S. Siba, T. Handa and H. This Bulletin, **26**, 364 (1953).

from a 500 watts tungsten lamp, operating at a constant voltage of 75 volts.

These condensed aromatic compounds are typical molecular crystals and have no impurities, that is, they are intrinsic semi-conductors. Therefore, their physical properties don't change by further steps of sublimation. This character is very advantageous for the measurement of photoconductivity compared with inorganic semi-conductors, such as Sb_2S_3 and CdS.

The optical absorption of solid state was observed by the LiF monochrometer. In this experiment, the organic substances were evaporated on a quartz plate or a glass one, as a thin layer, which had from 10 to 100 micron thickness.

Results and Discussions

Gudden and Pohl have described in their famous works[7], that a photoelectric current is separated into two types, viz., primary current and secondary current. The former is a motion of charges, electrons and holes, released throughout the illuminated volume by the action of photoelectrons and the latter is introduced with the contribution of the lowering of electronic barriers by the primary current, thus permitting the flow of additional electrons.

The photoelectric current observed here is proportional to the intensity of the incident light as shown in Fig. 3. This character is one of the most distinct properties of a primary current. Then, it may be reasonable to say that the observed photocurrent in this experiment is a primary current.

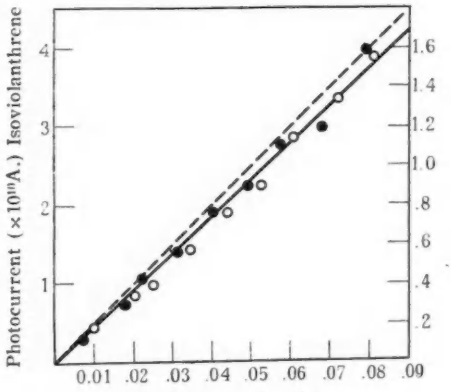


Fig. 3. Photoelectric current as a function of the intensity of illumination for ovalene photocell (—○—○—) and isoviolanthrene photocell (—●— - —●—) at 270 V. potential difference across these layers.

When "isoviolanthrene photocell" was illuminated by the white light (0.055 W./cm.²), the photoelectric current of this cell was changed with applied potential across the isoviolanthrene layer as shown in Fig. 4. When the thickness of film was from 50 up to 100 micron, then a 10^2 V. potential difference across the layer corresponded to 10^4 V./cm. This character was similar to the amorphous selenium film[8]. The photoelectric current increased nearly linearly with applied voltage and didn't indicate any saturation

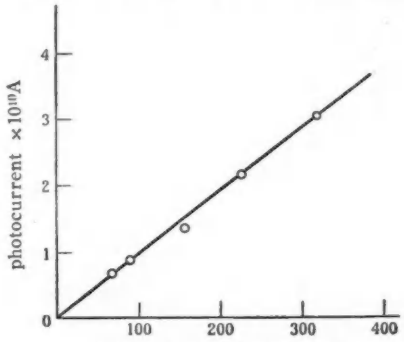


Fig. 4. Photoelectric current plotted against the Voltages applied across the isoviolanthrene photocell for the illumination of the white light (0.055 W./cm.²).

at the possible high voltage (270 V.). The ordinary semi-conductors, such as ZnS, have a saturated photocurrent at 10^3 V./cm[9].

The photocells of ten organic substances, described already, were made and the photoelectric current at 270 V. potential difference across these organic semi-conductive layers, which was illuminated at $10^{-3}-10^{-4}$ W./cm.² intensity monochromatized light, was measured. The spectral response of photoelectric current is shown in Fig. 5–7.

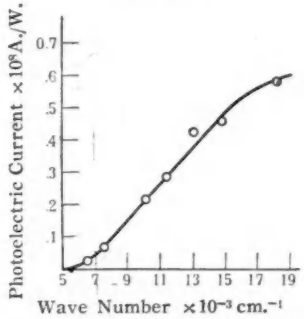


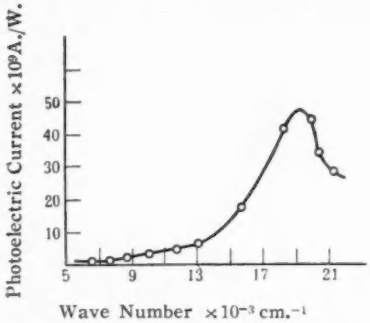
Fig. 5. Spectral response of photoconductivity for the flavanthrone photocell.

7) B. Gudden, "Lichtelektrische Erscheinungen," Julius Springer, Berlin, 1928.

8) P. K. Weimer and A. D. Cope, *R. C. A. Rev.*, **12**, 314 (1951).

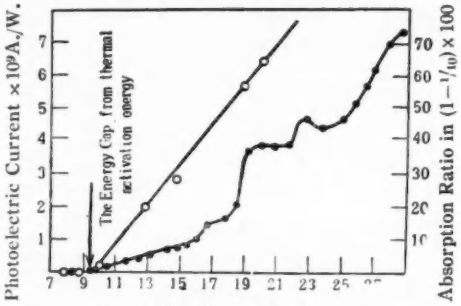
9) B. Gudden and R. Pohl, *Z. f. Phys.*, **17**, 331 (1923).

The photocurrent decreased as the wavelength of the incident light increased in each case, and the threshold was found. The value of light quantum in e.V. at each threshold is illustrated in TABLE I.



Wave Number $\times 10^{-3}$ cm.$^{-1}$

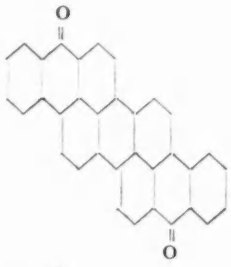
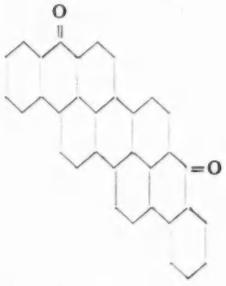
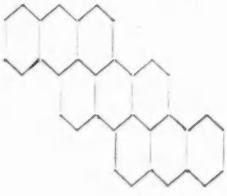
Fig. 6. Spectral response of photoconductivity for the isoviolanthrene photocell.



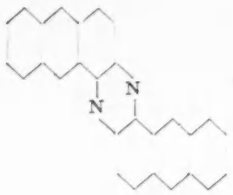
Wave Number $\times 10^{-3}$ cm.$^{-1}$

Fig. 7. Spectral response of photoconductivity and optical absorption curve for ovalene —○—○—○— photoconductive response, —●—●—●— optical absorption curve.

TABLE I. THE ENERGY GAP OF THE CONDENSED POLYNUCLEAR AROMATIC AND AZA-AROMATIC COMPOUNDS

Substance	Structure	Energy gap in e.V. unit: from photoconductivity	from optical absorption	from thermal activation energy
Isoviolanthrone		0.93	0.7—0.7_5	0.75
Violanthrone		0.84	0.7_5	0.78
Isoviolanthrene		0.85	—	0.82

Violanthrene	0.88	0.8	0.85
Ovalene	1.20	1.2	1.13
Pyranthrone	1.14	$0.8—0.8_5$	1.06
Pyranthrene	0.85	$0.7_5—0.8$	1.07
Flavanthrone	0.76	$0.7—0.7_5$	0.70
Indanthrone	0.74	0.6_5	0.63

Indanthrazine		0.80	0.6_5—0.7	0.66

The observed dark currents were changed with substances measured, with thickness of films and with other conditions. However, when the photocell was illuminated with the tungsten lamp, which had 0.1 W/cm² intensity, the ratio of photocurrent to dark current was about from 5 to 20 times. For example, the photocurrent and dark current of indanthrone were 5.14×10^{-11} A and 1.37×10^{-11} A, pyranthrone 19.6×10^{-11} A and 2.7×10^{-11} A and this ratio of "ovalene photocell" was very large, such as 140×10^{-10} A of photoelectric current and 1.54×10^{-10} A of dark current at room temperature. This is very

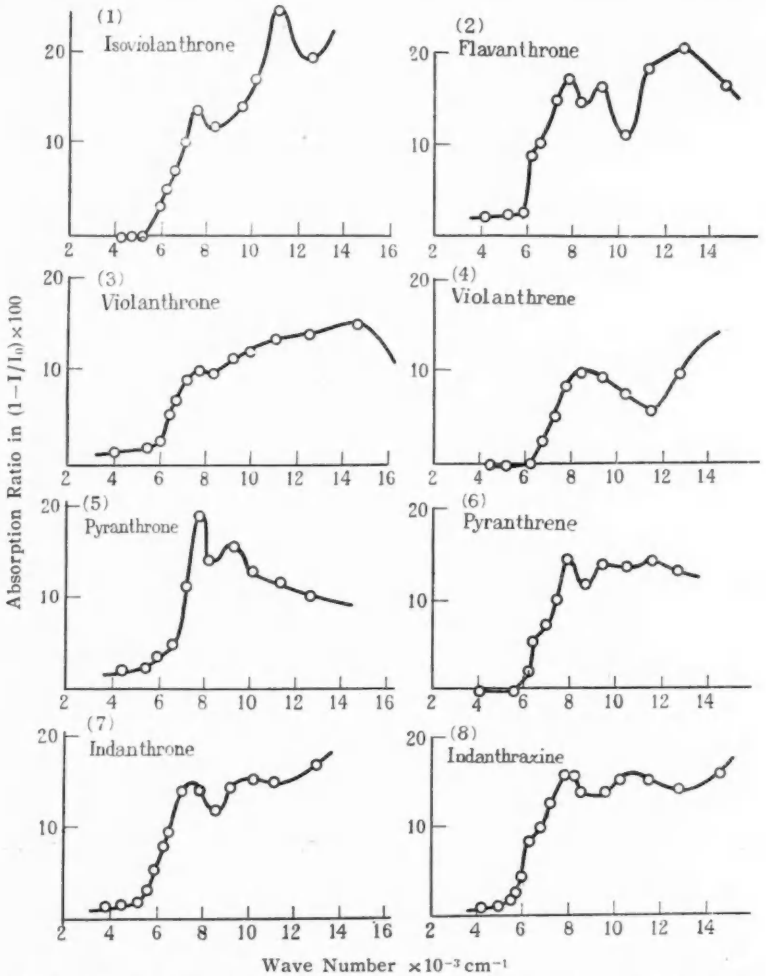


Fig. 8. Optical absorption of the organic semi-conductors. (1) isoviolanthrone, (2) flavanthrone, (3) violanthrone, (4) violanthrene, (5) pyranthrone, (6) pyranthrene, (7) indanthrone and (8) indanthrazine.

interesting when compared with the molecular structure.

These organic semi-conductors have no impurities—intrinsic semi-conductors. Then, assuming a crystal band structure, the threshold values correspond to the energy gap between the full band and the empty band.

To study the correlation between the photoconductivity and the optical absorption of crystals, the author has measured the absorption spectrum of layers of these organic substances. The spectral response of this character is shown in Fig. 8, and the threshold values are tabulated in TABLE I in e. V. unit. In TABLE I, results of photoconductivity, the optical absorption of solid and the temperature dependence of electrical conductivity satisfactorily coincide with each other. For example, these three characteristics of ovalene are shown in Fig. 7.

This will be due to the fact that the organic semi-conductors studied here are intrinsic ones having molecular lattice.

Summary

Photoconductivity and optical absorption in the solid state of the organic semi-conductors, that is, isoviolanthrone (I), violanthrone (II), isoviolanthrene (III), violanthrene (IV), pyranthrone (V), pyranthrene (VI), ovalene (VII), flavanthrone (VIII), indanthrone (IX) and indanthrazine (X) were measured. From the threshold values of the spectral response of the photoelectric current and optical absorption in the solid state, the energy gap between the full band and the empty band were estimated as (I) 0.93 eV, 0.7 eV, (II) 0.84 eV, 0.75 eV, (III) 0.85 eV, —, (IV) 0.88 eV, 0.8 eV, (V) 1.14 eV, 0.85 eV, (VI) 0.85 eV, 0.8 eV, (VII) 1.20 eV, 1.2 eV, (VIII) 0.76 eV, 0.75 eV, (IX) 0.74 eV, 0.65 eV, (X) 0.80 eV, 0.7 eV respectively. Also from the experimental facts that the photocurrent is proportional to the applied potential and to the light intensity, the author thinks that the photocurrent observed here is a primary current. These results, photoconductivity and absorption spectra, are in good agreement with that estimated from the temperature dependence of the electrical resistivity. It may be reasonable that this agreement is due to the fact that the organic semi-conductors studied here are intrinsic ones having molecular lattice.

The author expresses his hearty thanks to Prof. H. Akamatu for his kind direction of this study. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education, to which the author's thanks are due.

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Thermal Diffusion Factor of Hydrogen-Nitrogen Mixture

Kozo HIROTA*) and Kazuo SASAKI

(Received September, 10, 1953)

Introduction

Recently it becomes easy to discuss intermolecular potential by the theoretical and experimental development. Considering the fact that the effect of thermal diffusion is affected more sensitively by the intermolecular potential than any other transport phenomena, such as viscosity, ordinary diffusion, etc., it will be interesting to treat the effect in relation to this standpoint. Actually, several authors have already attacked the problem theoretically[1], but it seems to us that they did not extend their research in such details so far as to check whether or not the experimental data agree with their theory over the entire range of composition. It was, therefore, attempted in the present paper to treat the problem from another direction, adopting hydrogen-nitrogen mixture as the system to be studied, because it has been the most studied of all the binary mixtures.

Theoretical Consideration

To begin with, thermal diffusion factors α of this system were collected from the reports hitherto published, instead of k_t, for

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1) S. Chapman, *Proc. Roy. Soc.*, A **177**, 38 (1940). R.C. Jones, *Phys. Rev.*, **58**, 111 (1949); **59**, 1019 (1941). M. Kotani, *Proc. Math.-Phys. Soc. Japan*, **24**, 76 (1942). T. Kihara and M. Kotani, *ibid.* **25**, 602 (1943). Hirschfelder, Bird, and Spotz, *Chem. Rev.*, **44**, 205 (1949). K. E. Grew, *Proc. Roy. Soc.*, A **189**, 402 (1947), K. E. Grew, *Proc. Phys. Soc.*, **62**, 655 (1949). E. R. S. Winter, *Trans. Faraday Soc.*, **46**, 81 (1950), etc.

the reason that the former constant varies less against composition than the latter*).

All these values, except those which were obtained at the mean temperatures much lower than 0°C, are plotted in solid circles against molar fraction of hydrogen (c), as shown in Fig. 1, where some of them had to be determined by evaluating from the data of original papers. The four points designated in the triangle are those determined under 1-12.6 atm. pressure recently by Hirota and Kobayashi[2], using the Clusius-Dickel column, and the numerals attached to them indicate the pressure under which the experiment was carried out. It will be important that these data at high pressure also coincide with those obtained at ordinary pressure, though, according to Becker, it will increase to some extent under 80 atmospheric pressures[3].

If we exclude, for the time being, the values marked by the triangle and the open circle which will be explained in the present paper, it is evident that the observed α's increase linearly with hydrogen concentration**), but there is a tendency for their mutual difference to increase more greatly at the same time, especially in the concentration above $c=0.80$. Such a dispersed state of the results cannot be caused by the temperature difference among the measurements, because the difference is too small to be explained on both theoretical and experimental grounds, while also it cannot be caused by the slight pressure difference[4], as described above.

On the other hand, the first approximate values[5] of α were calculated by using the Lennard-Jones 12:6 potential:

$$V(r)=4\epsilon\left\{\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r}\right)^{6}\right\}$$

(ϵ is the depth of the potential energy minimum and r_0 is the low velocity collision diameter). The difficult numerical calculation could be avoided by use of the tables given by Hirschfelder, et al.[1,6], the basic constants required in the procedure are as follows:

$\epsilon(H_2)/k=33.3°K$,
$r_0(N_2)=2.968Å$ (from viscosity),
$\epsilon(N_2)/k=91.46°K$,
$r_0(N_2)=3.681Å$ (from viscosity),
and $\epsilon(N_2\sim H_2)/k=47.8°K$,
$r_0(N_2\sim H_2)=3.325Å$.

(k is the Boltzmann constant.) The temperature was assumed to be 321.6°K in the calculation.

The calculated result is shown by the full line in Fig. 1, where the dotted is the one when a rigid sphere potential is adopted in calculation, using 2.730Å, 3.756Å and 3.243Å as the collision diameter of hydrogen, nitrogen and nitrogen-hydrogen, respectively. It is clearly shown, as ought to be, that the latter cannot reproduce the experiment, while that of the Lennard-Jones potential can reproduce the experimental values better. But even this potential cannot give the decreasing tendency of α in high hydrogen concentration.

Experiment and Discussion

Considering the situation, thermal diffusion

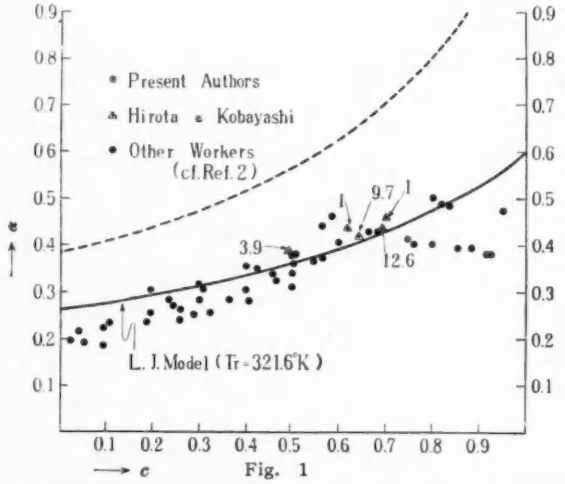

Fig. 1

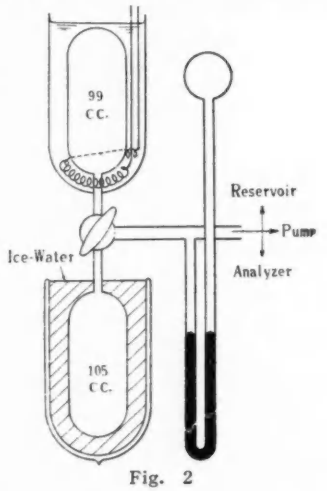

Fig. 2

*) Between a and kt, there is a relation: $kt=ac(1-c)$, where c is the concentration in molar fraction.

**) The present data of Hirota and Kobayashi differ slightly with those of the former report, due to the accurate determination done later.

2) K. Hirota and Y. Kobayashi, *J. Chem. Phys.*, **21**, 246 (1953).

3) E.W. Becker and A. Schulzeff, *Naturw.*, **35**, 219 (1948).

4) Regarding this system, E. Whalley (private communication) obtained the result that separations at one atmosphere and 1 mm.Hg. seem to be identical within a few percent, if two bulbs were maintained for a sufficient time at 295°K and 427°K, respectively.

5) Chapman and Cowling, "Mathematical Theory of Non-Uniform Gases" (1939).

6) Hirschfelder, Bird and Spotz, *J. Chem. Phys.*, **16**, 968 (1948).

factors of relatively high hydrogen concentration were determined by the two-bulb-method. The main apparatus consisted of two bulbs (about 100 cc.) as shown in Fig. 2. Higher and lower temperatures were kept at 0°C. and 100°C. by ice-water and boiling water, respectively. The purity of the samples was tested mass-spectrometrically, and the impurity, being mostly oxygen, was found to be less than 0.1%. The concentration of hydrogen in the samples was analyzed by the volume decrease, oxidizing it with CuO heated at 300°C. During sampling care was taken that no concentration change should occur due to the difference of the diffusion rate of hydrogen and nitrogen through the tubing. Each experiment was carried out for a much longer time—five or more times —than the relaxation time (ca. 1.5 hours) defined by

$$t_r=\left(\frac{L}{\rho DS}\right)\left(\frac{mm'}{m+m}\right)\cdot\frac{1}{2}\cdot\left(\frac{T+T'}{T-T'}\right)\cdot\ln\left(\frac{T'}{T}\right),^{7)}$$

where L, length of the connecting tube = 11 cm;
ρ, density;
D, diffusion coefficient;
S, cross section of the tube = (π/4.0 cm^2);
$m(m')$, mass in the reservoir of higher (lower) temperature;
$T(T')$, higher (lower) temperature.

The experimental data and α obtained from them are shown in table 1 and by the open circles in Fig. 1 (c=0.74, 0.79, 0.88 and 0.89). It is shown that the experimental points are still lower than the theoretical line. Therefore, the discrepancy already mentioned in the region of higher concentration does not disappeared, but rather seems

TABLE I

Mean hydrogen conc. (molar fraction)	Separation (molar fraction)	Thermal diffusion factor α
0.741_4	0.023_8	0.39_7
0.792_8	0.020_4	0.39_8
0.879_5	0.010_7	0.32_5
0.890_9	0.010_5	0.34_4

to be confirmed. Considering the fact that the potential adopted by the present paper holds fairly well to other transport phenomena, such an unexpected disagreement between theory and experiment may be brought out by the use of Chapman's first approximate formula of α besides as well as becauce of the incompleteness of the intermolecular potential adopted.

Summary

The thermal diffusion factor of the nitrogen-hydrogen system has been discussed theoretically. It has been found that the Lennard-Jones potential can reproduce the experimental result, if the hydrogen concentration is below 0.8 in molar fraction. Each experiment done by use of the two-bulb-method in hydrogen concentration 0.74−0.89 has given similarly smaller value than expected theoretically. Such discrepancy may be caused by the theoretical formula of α as well as by the incomplete intermolecular potential.

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7) H. Brown, *Phys. Rev.*, **58**, 661 (1940).

Studies on the Degradation of Yeast Ribonucleic Acid by Lanthanum Hydroxide. On the Existence of a Resistant Fraction

By Michio SHIMOMURA

(Received September, 11, 1953)

Ribonucleic acid (RNA) was shown in the previous paper[1] to be hydrolysed almost completely into nucleosides and inorganic phosphate by the action of lanthanum hydroxide. However, it was still ambiguous as to whether the nucleic acid is completely dephosphorylated or not, since it is a compound of high complexity. In the case of the enzymatic degradation of RNA by ribonuclease (RNase), a non-dialysable residue has been known to remain which comprises 15 to 50 per cent of the original[2)3)], and this fact has offered a clue for the research on the ribonucleic acid structure[4)5)6)].

1) M. Shimomura and F. Egami, This Bulletin, **26**, 253 (1953).

2) H. S. Loring, F. H. Carpenter and P. M. Roll, *J. Biol. Chem.*, **169**, 601 (1947).
3) G. Schmidt, R. Cubiles, B.H. Swartz and S.J. Thannhauser, *J. Biol. Chem.*, **170**, 759 (1947).
4) E. Chargaff, *J. Cell. Comp. Physiol.*, **38**, Supplem. 1, 41 (1951).
5) G. Schmidt, R. Cubiles and S. J. Thannhauser, *J. Cell. Comp. Physiol.*, **38**, Supplem. 1, 61 (1951).
6) B. Magasanik and E. Chargaff, *Biochim. Biophys. Acta*, **7**, 396 (1951).

In the work to be described it was found that the action of lanthanum hydroxide can not lead to the perfect dephosphorylation of RNA, but that a resistant fraction (LaRF) remains. Some properties of the resistant fraction were studied and compared with those of the ribonuclease resistant fraction (RNaseRF).

Materials and Analytical Methods

Yeast Ribonucleic Acid A commercial sample of RNA prepared from brewer's yeast by the method of Clark and Schryver[7] (Kirin Institute) was used after purification by the usual chloroform method.[8] The phosphorus content of the purified preparation was 8.0 per cent.

Lanthanum Carbonate The purification procedure of the carbonate has been described previously.

Ribonuclease The enzyme was extracted from calf. spleen and partially purified by the method of McDonald[9] up to the step of B Fraction. The preparation was freed from salt by washing with aqueous ethanol and then with absolute ethanol and dried in vacuum. Yeast RNA liberated no inorganic phosphate by the action of this preparation.

Ribonuclease Resistant Fraction 200 mg. of RNA were digested with 10 mg. of RNase in 15 cc. of M/100 magnesium sulfate. The digestion proceeded at 37° for 3 hours and occasional addition of dilute alkali maintained the mixture at *p*H 7—8. A 5 cc. aliquot was then removed and the residual 10 cc. of digested nucleic acid solution was dialysed through cellophane first against 500 cc of 2M solution of sodium chloride[10] then against 1 litre of distilled water for 24 hours, respectively. The estimation of the phosphorus content of the dialysis residue showed that 80 per cent of the original material had been removed.

Analytical Methods The same methods as those in the previous paper[1] were used.

Methods and Results

Estimation of LaRF The reaction mixture, similar to that described in the previous paper[1], was constructed as follows: 200 mg. of lanthanum carbonate were suspended in distilled water in a 50 cc. Erlenmeyer flask and dissolved by adding hydrochloric acid. On adjustment of the solution to *p*H 8.5 by the addition of aqueous ammonia, lanthanum hydroxide was precipitated. To this suspension a RNA solution containing 10.8 mg. of the purified material, 10 cc. of M/5 borate buffer solution at *p*H 8.5 and then water were added till the final volume was 40 cc. The reaction proceeded at 80°.

Preliminary experiments showed certain difficulties in the estimation of undephosphorylated RNA from the difference between the total and the inorganic phosphorus of the reaction mixture, since the difference was small. Fortunately, however, it was found that the liberated nucleosides are not adsorbed on lanthanum hydroxide, a powerful precipitating agent of nucleic acid. Therefore, the measurements were carried out in the following manner. A 4 cc. sample was withdrawn at intervals and centrifuged. The precipitates were washed twice with 8 cc. of dilute lanthanum hydroxide suspension respectively in order to remove nucleosides, and analysed for RNA by the orcinol method. It is a well known fact that in this colorimetric method the color is given by purine-bound ribose. The results of the experiment, which are presented in Table, 1, have been calculated on the assumption that the purine/pyrimidine ratio of the undephosphorylated fraction is the same as that of the original material.

TABLE I

ESTIMATION OF UNDEPHOSPHORYLATED RNA

Time (hrs.)	Undephosphorylated RNA (%)
40	7.8
56.5	7.3
99	5.9

It can be seen in TABLE I that some amounts of RNA remain undephosphorylated, although they are not completely stable to the action of lanthanum hydroxide. At any rate, they are remarkably resistant in view of the fact that 99.9 per cent dephosphorylation might be expected in 40 hours from the calculation based on the first order reaction constant of the reaction up to 85 per cent dephosphorylation.

Preparation of LaRF An RNA solution containing 15 g. of the material was mixed with a lanthanum hydroxide suspension which was prepared from 30 g. of the carbonate. The final volume was about 1 litre. This mixture was adjusted at *p*H 8.5 by the addition of aqueous ammonia and maintained at 80° for 40 hours. The occasional addition of ammonia prevented the lowering of *p*H of the mixture during the hydrolysis. The precipitate was subsequently filtered while warm, washed with hot water to remove nucleosides and suspended in about 150 cc. of 5 per cent solution of sodium bicarbonate which had previously been adjusted at *p*H 8 with dilute hydrochloric acid. After standing for about 2 hours, lanthanum carbonate was removed by centrifugation. The clear supernatant, which contained RNA, was made slightly acid (*p*H 5) with acetic acid, freed from the excess of bicarbonate by a current of air under reduced pressure and neutralized with ammonia.

The above procedure was repeated once more with lanthanum hydroxide prepared from 10 g. of the carbonate. LaRF solution thus obtained contained a small amount of inorganic phosphate, which was removed by the addition of a small amount of lanthanum hydroxide and subsequent centrifugation. The final yield of LaRF was calculated on the basis of its phosphorus yield to be about 1.5 per cent of the original material.

Analysis of LaRF The LaRF solution prepared as described contained about 15 per cent of

7) G. Clark and S. B. Schryver, *Biochem. J.*, **11**, 319 (1917).
8) M. G. Sevag, D. B. Lackman and J. Smolens, *J. Biol. Chem.*, **124**, 425 (1938).
9) M.R. McDonald, *J. Gen. Physiol.*, **32**, 39 (1948).
10) R. Markham and J. D. Smith, *Biochem. J.*, **52**, 565 (1952).

DNA (TABLE II); it may be explained by the facts that DNA is not dephosphorylated by lanthanum hydroxide, and that yeast RNA preparation is generally contaminated by a small amount of DNA. Its purine-bound ribose/RNA-P was much greater than that of the original RNA.

TABLE II
COMPARISON OF ANALYTICAL FIGURES OF VARIOUS FRACTIONS

	DNA-P	Purine-bound Ribose
	Total P %	RNA-P mol./mol.
LaRF	15	1.08
RNaseRF		0.80
RNA		0.50 (Standard)

DNA-P was measured by the diphenylamine method on the assumption that the purine/pyrimidine ratio was 1. Purine-bound ribose was calculated from the color intensity of the orcinol test on the assumption that the original RNA preparation contained equimolecular purine-and pyrimidine-bound riboses. RNA-P was taken as the difference between total P and DNA-P.

Dephosphorylation of Various Fraction by Lanthanum Hydroxide The dephosphorylation of LaRF by lanthanum hydroxide was very slow (Curve 1), and this was also the case even after digestion by RNase (Curve II), while RNaseRF (Curve III) and the whole digest of RNA by RNase (Curve IV) were dephosphorylated as easily as RNA itself.

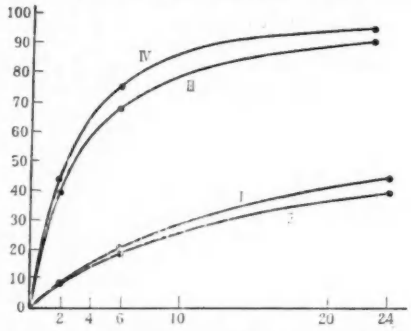

Fig. 1. Dephosphorylation of various fractions by lanthanum hydroxide. The preparation of RNaseRF and the whole digest of RNA by RNase are described in the text. The digestion of LaRF by RNase; LaRF solution containing about 400 μg. of phosphorus was incubated with 1 mg. of RNase at pH 7.0—7.5 and 37° for 3 hours. The incubations with lanthanum hydroxide were carried out at pH 8.5 and 80°. (The methods were described in the previous paper.)

Discussion

In the present experimental conditions, LaRF was not completely resistant to the action of lanthanum hydroxide. Anyhow, the observations presented here indicate that the structure of a certain specific portion of RNA is different from the rest.

The recent study in this laboratory showed that RNA becomes, by methylation of the hydroxyl group at C_2' of the sugar residue, as lanthanum hydroxide resistant as DNA, which has no hydroxyl group at C_2', and that the methylated RNA is not attacked by RNase[11]. In this connection, it is interesting that LaRF itself and LaRF treated with RNase were not easily dephosphorylated by lanthanum hydroxide, although the resistibility of LaRF to lanthanum hydroxide was not so great as that of the methylated RNA. It may be supposed that the hydroxyl group at C_2' might be masked in some way in LaRF. Anyhow this fact will offer a new clue for the elucidation of the structure of RNA.

Summary

1. Yeast ribonucleic acid is, as reported in the previous paper, hydrolysed almost completely into nucleosides and inorganic phosphate by lanthanum hydroxide, but the remaining fraction is considerably resistant to the action of the hydroxide.

2. Purine-bound ribose/RNA-p ratio of the resistant fraction is about 1.

3. Even after the treatment with ribonuclease, dephosphorylation of the resistant fraction by lanthanum hydroxide is not easy.

4. The ribonuclease resistant fraction is dephosphorylated by lanthanum hydroxide as easily as ribonucleic acid itself.

The present author wishes to express his thanks to Professor Fujio Egami for suggesting this investigation as well as constant encouragement in the course of the work. A part of the cost of this investigation was defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to whom I extend my thanks.

Chemical Institute, Faculty of Science, Nagoya University, Nagoya

11) F. Egami, H. Ishihara and M Shimomura, *Z. Physiol. Chem.*, **295**, 349 (1953).

Dielectric Behaviours of Hydrated Crystals I. Strontium Formate Dihydrate, Potassium Copper (II) Chloride Dihydrate and Ammonium Copper (II) Chloride Dihydrate[1]

By Ryôiti KIRIYAMA and Hideko IBAMOTO

(Received September 21, 1953)

Introduction

The investigations of the dielectric behaviours of the hydrated crystals will render some strong clues about the binding state of the water molecules in the crystal lattices. In these measurements, however, it is difficult to obtain reliable data owing to some sorts of lattice imperfections, especially liquid inclusions or efflorescent nuclei, and the surface leakage originated probably from the adsorbed water molecules. For the purpose of avoiding such phenomena, it will be desirable to use large, transparent, single crystals which make it possible to minimize these troublesome effects. In the present paper, the temperature and frequency dependences of the dielectric properties of one rhombic crystal, strontium formate dihydrate, $Sr(HCO_2)_2 \cdot 2H_2O$ and two isomorphous tetragonal crystals, potassium copper (II) chloride dihydrate, $K_2CuCl_4 \cdot 2H_2O$ and ammonium copper (II) chloride dihydrate, $(NH_4)_2CuCl_4 \cdot 2H_2O$ which contain directly coordinated water molecules to the divalent metal ions are reported and the anisotropies of the permittivities of the cupric salts are discussed.

Experimental

Crystals and Specimens of Strontium Formate Dihydrate. As the temperature dependence of the solubility of this anhydrate in water is rather small, a single crystal of this substance can be obtained by slow cooling, together with slow vaporization from the seed crystal placed on the bottom of a glass vessel, filled with a slightly supersaturated aqueous solution, which is kept in an air-thermostat with a regulator of $\pm 1°$ in the range of 40–30°C.[2] Cutting and grinding these transparent large single crystals perpendicular to three crystallographic axes, we obtain suitable specimens of about 1.5×1.5 cm^2. in area and 1.0–1.5 mm. in thickness in each case. These slices are pasted by tin foils with vacuum grease on both sides. Then this specimen is inserted into the plate condenser mentioned below.

Crystals and Specimens of Potassium Copper (II) Chloride Dihydrate and Ammonium Copper (II) Chloride Dihydrate. These crystals are grown by slow cooling of the supersaturated aqueous solutions by the same process mentioned above. But the temperature dependences of the solubilities being rather steep, it is necessary to regulate the temperature-fluctuation within less than ±0.1°. Consequently, the growing vessels are placed in a water-thermostat and the temperature is carefully controlled. Large crystals thus obtained are cut and ground to form suitable slices which are perpendicular to two crystallographic axes. Among these specimens we select nearly perfect, single crystals which are scarcely optically anomalous and not twinned according to the examination using a polarizing microscope. The slice is directly put between silver-coated brass electrodes forming a crystal condenser in the measuring circuit.

Equipment. The crystal condenser for the measurement at room temperature is a somewhat improved type of the previously used condenser in our laboratory,[3] and the permittivities of the crystal are determined from the ratios of the capacities of the specimens to those of the artificial rock salt of which permittivity is adopted at 5.62 as the standard value.[4] This rock salt was prepared by Stockberger's method in our laboratory.

The cell for the observation of the temperature dependence is also an improved type of that previously reported.[3] The temperature of the specimen in the cell is measured by a copper-constantan couple in the limit of ±1°C. The heating rate is about 0.2°/min. in every case. For the purpose of avoiding the condensation of water vapour upon the crystal surface when the cell is cooled down, a small member of calcium chloride grains have been spread on the bottom of the cell.

The measurements at audio-frequencies are carried out using a capacity-resistance bridge with RC-type oscillator. In these cases, there are no remarkable dispersions between 20 kc–1 kc, thus the measurements are performed mainly at 5 kc.

1) This paper was partly presented at the annual meeting of the Crystallographic Society of Japan on May 14, 1950 and partly at the meeting of the Chemical Society of Japan on Sept. 20, 1952 (a symmposium on structural chemistry) and also on Nov. 17, 1952 (a symmposium on complex salt).

2) R. Kiriyama, Studies on the velocities of crystal growth I. The growth condition of the single crystal of strontium formate dihydrate, *J. Chem. Soc. Japan*, **70**, 260 (1949), in Japanese.

3) T. Suita, K. Suenaga and I. Nitta, Abstract of the Electrical Engineering Section of the 4th general meeting of Nippon Kogakukai on April, 1940, page 18.

4) K. Höjendahl, *K. Danske Vidensk. Selskab.*, **16**, No. 2, (1938).

The measurements at radio-frequencies are carried out by a resonance circuit and the dielectric losses are obtained by resistance-substitution. The frequencies used are 600 kc. and 3 Mc. stabilized by quartz oscillators.

Result

Strontium Formate Dihydrate. The permittivities along three crystallographic axes at a room temperature are as follows,

$$\varepsilon_a=5.2,\quad \varepsilon_b=4.9,\quad \varepsilon_c=4.3$$

In these cases, the frequency dependences between 5 kc. and 3 Mc. are not observable, and these values may be more precise than those previously reported by one of the authors.[5]

The temperature dependences between −170°C. and the dehydration point at 3 Mc. are shown in Fig. 1. The temperature coefficients of the permittivities along three axes are very small and it shows a horizontal straight line up to about 70°C. in every case. But the permittivities show slightly decreasing tendencies of at least 1% when the temperature rises above about 70°. However the permittivities increase suddenly at 75° and the crystal collapses, followed by dehydration of the total water of crystallization.

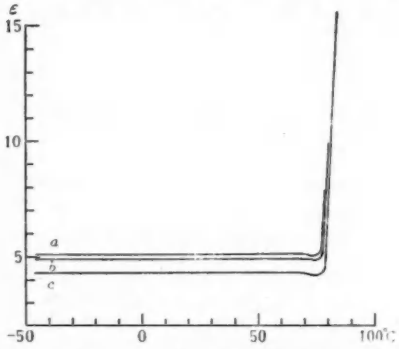

Fig. 1. Strontium formate dihydrate: Anisotropy and temperature dependences of the permittivities along its three crystallographic axes.

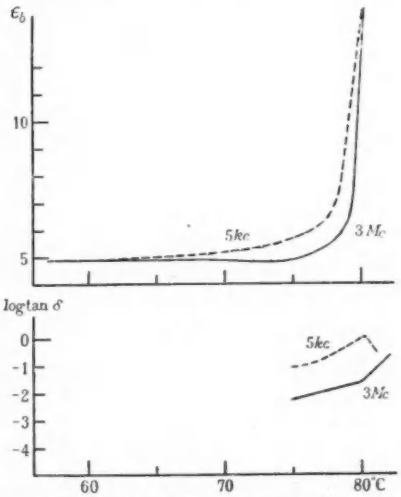

Fig. 2. Strontium formate dihydrate: Dispersion at 3Mc. and 5kc.

5) R. Kiriyama, *Kagaku*, **17**, 239 (1947), in Japanese.

The change and dispersion of the dielectric behaviour before and after the dehydration are shown in Fig. 2 in which the curves along *b*-axis are picked up as an example. The permittivity at 5 kc is higher than that at 3 Mc above 65° and the dielectric loss at 5 kc is also far greater than that at 3 Mc. The cause of such a high dielectric loss will be attributed to the surface conduction of the dehydrated polycrystals. Actually, it is confirmed that the loss diminishes when a thin mica foil has been inserted between the crystal specimen and one of the electrodes.

Potassium Copper (II) Chloride Dihydrate and Ammonium Copper (II) Chloride Dihydrate. The permittivities at room temperature are as follows,

$K_2CuCl_4\cdot 2H_2O$: $\varepsilon_a=8.5,\ \varepsilon_c=5.1$
$(NH_4)_2CuCl_4\cdot 2H_2O$: $\varepsilon_a=7.2,\ \varepsilon_c=5.6$

There are no detectable dispersions between 3 Mc. and 5 kc at room temperature. But, it is remarkable that, in spite of the isomorphous structure, the potassium salt shows greater anisotropy than that of ammonium salt.

The temperature dependences of the permittivities and the losses of both salts are shown in Fig. 3 and 4. The temperature coefficients of the permittivities $\frac{1}{\varepsilon}\left(\frac{d\varepsilon}{dT}\right)$ are obtained from these experimental curves.

$K_2CuCl_4\cdot 2H_2O$: −170 — −20°C. (3 Mc. and 5 kc.)
along *a* nearly zero; along *c* 2.2×10^{-4}
$(NH_4)_2CuCl_4\cdot 2H_2O$: −170 — −130°C. (3Mc. and 5 kc.)
along *a* -7×10^{-4}; along *c* 9×10^{-4}
−130 — 0°C. (3 Mc. and 5 kc.)
along *a* nearly zero; along *c* nearly zero
0 — 100°C. (3 Mc. and 5 kc.)
along *a* 1.7×10^{-4}; along *c* 2.2×10^{-4}

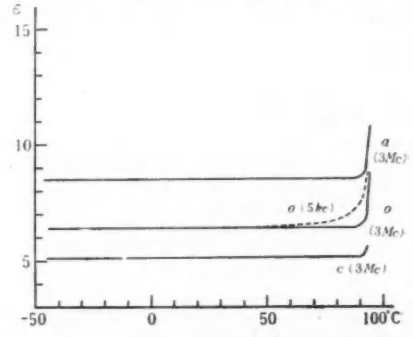

Fig. 3. Potassium copper (II) chloride dihydrate: Temperature dependences of the permittivities and the dispersion perpendicular to *o*(111) -plane.

100 — 125°C. (3 Mc.)
along a 1.1×10^{-3}; along c 0.6×10^{-3}
100 — 125°C. (5 kc.)
along a 6.5×10^{-3}; along c 6×10^{-3}

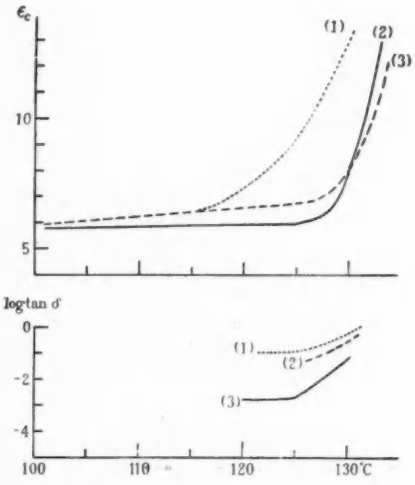

Fig. 4. Ammonium copper (II) chloride dihydrate: Temperature dependences of the permittivities and the dielectric losses; (1) 5kc., direct; (2) 5kc., both sides mica foils; (3) 3Mc., one side mica foil.

Thereupon, in the case of the ammonium salt at low temperatures, we found a rather curious anisotropy of the temperature coefficients which are negative in a-direction and positive in c-direction. The dielectric behaviour of the potassium salt is analogous to that of strontium formate dihydrate which shows no remarkable change up to the dehydration temperature. Especially, in the case of this potassium salt, it shows also a little decreasing tendency at 3 Mc. before the dehydration occurs.

The dehydration of the ammonium salt takes place at a considerably higher temperature than that of potassium salt and this temperature difference will cause some effects originated in the dehydrated water molecules. In the experiments of the ammonium salt, we have often met with the emergence of electrochemical reactions between the specimen and the brass electrodes of which the silver-coating had been perhaps imperfect.

For the purpose of investigating both effects of the surface conduction and the electrode reaction, we have tried to observe the temperature dependences of the specimens in the following ways.

(1) The specimen was directly put between two electrodes.
(2) A mica foil was inserted between the specimen and the lowerside electrode.
(3) Mica foils were inserted between the specimen and two electrodes to separate the effect of d.c. conduction.

Three examples along c-direction of these experiments in the neighbourhood of the dehydration temperature are plotted in Fig. 4.

Discussion

The crystal structure of strontium formate dihydrate was analysed by I. Nitta and K. Osaki[6]. According to their result, one water molecule is coordinated directly to the strontium ion but the other is packed in the lattice surrounded by oxygen atoms and water molecules with hydrogen bond distances. The anisotropy of the permittivities is rather small. This may be expected from the less anisotropic arrangement of the constituent atoms, radical ions and molecules. The negligible smallness of temperature and frequency dependences of permittivities may suggest that there exist fairly strong hydrogen bonds in the lattice and that no rotation-like motions of the water molecules or, unquestionably, of the formate ions will occur up to the collapse of the lattice accompanied with the dehydration of the water of crystallization.

The slight depression of the permittivities immediately below the dehydration temperature at 3 Mc. may be attributed to the loosening of the hydrogen bonds as in the case of the predehydration of copper sulphate pentahydrate[7]. But it is questionable whether the larger value at 5 kc in the same temperature region is a true dispersion caused by some rotation-like motion or originated by slight conduction on the crystal surface.

The abrupt increases of the permittivities due to the surface conduction at the dehydration temperature are analogous to many hydrated salts observed by us.

The crystal structures of both potassium and ammonium copper (II) chloride dihydrates are isomorphous and the perspective is shown in Fig. 5[8]. In this structure, $[CuCl_2(H_2O)_2Cl_2]$ rhombic octahedron is found, but we ought to adopt the planar rhombic $[CuCl_2(H_2O)_2]$ group parallel to c-axis rather than the rhombic planar $[CuCl_2Cl_2]$ group perpendicular to the c-axis as the copper (II)-complex ion in both crystals from the evidences of the atomic distances between the central Cu-atom and the ligands determined by the structure analysis.

Contrary to our expectation based on this isomorphic structure, there is found a larger anisotropy of the permittivities of the potassium salt than of the ammonium salt. The

6) I. Nitta and K. Osaki, read before the annual meeting of the Chemical Society of Japan, April 5, 1947.
7) R. Kiriyama and H. Ibamoto, This Bulletin, **25**, 359 (1952).
8) S.B. Hendricks and R.G. Dickinson, *J. Am. Chem. Soc.*, **49**, 2149 (1627); L. Chroback, *Z. Krist.*, **88**, 35, (1934).

most reliable reason for this discrepancy may be due to the atomic polarization of the hydrogen atom of the water molecule which

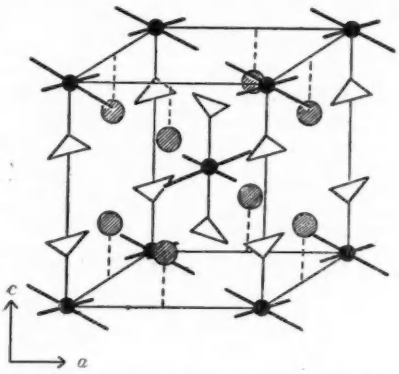

Fig. 5. The crystal structure of $K_2CuCl_4 \cdot 2H_2O$; Cu-black circle; K-hatched circle; H_2O-triangle; Cl is omitted but thick full lines indicate Cl—Cl distances in the orthorhombic octahedron.

has some different interactions in every lattice of both salts. It has been confirmed that the proton-proton distances were 1.62 ± 0.02Å in the potassium salt and 1.59 ± 0.02Å in the ammonium salt by means of the proton magnetic resonance experiments[9]. These values are considerably greater than that of the free water molecule, 1.51Å, determined by the spectroscopic method. The larger discrepancy found in the potassium salt may be caused by the fact that there is a stronger interaction between the O-H···Cl system in two neighbouring $[CuCl_2(H_2O)_2Cl_2]$ octahedrons. Moreover, the protonic polarization in the hydrogen bond is larger in the lateral direction of the bond axis than in the direction parallel to the line joining the two electronegative atoms as found in some crystals which contain O-H···O hydrogen bond systems in their crystal lattices[10]. Thus the stronger hydrogen bond of O-H···Cl in the potassium salt causes a larger anisotropy of the permittivity than that of the ammonium salt. Also this effect will clarify the difference of the dichroisms of the potassium and ammonium salts. The fact that one is strong and the other is weak respectively, is due to the difference of the bond strengths between the copper atom and the ligand water molecule. In the potassium salt, the copper-water bond is weaker than that of the ammonium salt owing to the stronger O-H···Cl bond mentioned above, therefore, the rhombic $[CuCl_2Cl_2]$ group on the *c*-plane will have more covalent nature than that of the ammonium salt. This difference of the bond nature, in other words, the polarization of the electron cloud of the chlorine atom will result in a stronger dichroism of the potassium salt than that of the ammonium salt.

The temperature dependences of the permittivities of the potassium salt are very small in a wide temperature range. And the slight dispersion above 50–60°C. may be attributed to the slight orientation of the dipoles of the water molecules occupying disordered lattice points which must often exist in this optically anomalous crystal. And, in this connection, it is noticeable here that there has been no temperature change of the biaxial interference figure of this optically anomalous crystal up to the dehydration temperature, therefore, this optical anomaly is not attributable to the somewhat regular misfit of the water molecules in the lattice. The sudden increase at the dehydration temperature is due to some conductive effects as in the case of the strontium formate dihydrate mentioned above.

In the case of the ammonium salt, the temperature dependences are analogous to that of the potassium salt and the principal explanation of these behaviours will be analogous to that above discussed. The reason for the slight negative temperature coefficient along *a*-axis at low temperatures, is not made clear at present, but it is noticeable that such a tendency is found also in ammonium mercury (II) chloride monohydrate and not in postassium mercury (II) chloride monohydrate[11].

In conclusion the authors wish to express their thanks to Prof. I. Nitta for his encouragement and suggetions during this work. The expense of this work was defrayed partly from the Scientific Research Grant from the Ministry of Education, to whom I extend my thanks.

Department of Chemistry, Faculty of Science, Osaka University, Nakanoshima, Osaka

9) J. Itoh, R. Kusaka, Y. Yamagata, R. Kiriyama and H. Ibamoto, *Physica*, **19**, 415, (1953).

10) In gypsum by the authors and in resorsinol and pentaerysritol by S. Yabumoto and R. Kiriyama; These results will be published shortly.

11) The results of these mercury (II) salts will be published in the following paper shortly.

Oxidation of Carbon Monoxide on Silver Surface

By **Noboru YAMADA**

(Received October 9, 1953)

Introduction

Kinetic studies on a catalytic reaction with the same catalyst have often shown different results by different investigators. On the oxidation of carbon monoxide with silver as catalyst, Benton and Bell[1] showed that the reaction rate was proportional to the pressure of carbon monoxide and independent of the oxygen pressure. On the other hand, Titani et al.[2] showed that the reaction rate was proportional to the oxygen pressure and independent of the carbon monoxide pressure. In both cases the reaction rate was measured by the flow method. The catalyst used by Benton and Bell was the reduced silver catalyst, silver powder prepared by reduction of silver oxide with hydrogen, and those used by Titani et al. were the reduced silver powder and electrolysed silver powder obtained by the electrolysis of acidic silver nitrate solution. The temperature range of experiment was 80–140°C with Benton and Bell, and 150–450°C with Titani et al. Thus the results so obtained by these investigators were inconsistent with each other.

The main aim of the following experiments have been to determine which was the real case, and to make clear why those conflicting results were obtained by the investigators.

Experimental

The measurements of the reaction rate were made by the flow method. The apparatus and procedure employed were almost the same as those used by Titani et al.[2]

Carbon monoxide was generated by dropping formic acid on hot concentrated sulfuric acid. Oxygen was obtained electrolytically from sodium hydroxide solution. Each gas was purified in the usual manner, and stored over water in each reservoir. They were forced out of each reservoir under pressure, dried in the liquid oxygn traps, their flow rate controlled by the glass capillary tubes and inserted wires, and mixed before the entrance of the reaction tube. The total flow rate was fixed at 20 cc. (0°C, 760 mm. Hg.) per min. Controlling the flow rate of each gas, mixed gas having various proportion of carbon monoxide and oxygen were passed over the catalyst at atmospheric pressure. The reaction tube of hard glass was 16 mm. in inside diameter and 230 mm. in length. In the middle of the tube 4 g. of the catalyst was packed ca. 20 mm. in length. The reaction tube was heated by a cylindrical electric furnace.

Both catalysts, the reduced silver powder prepared by reduction of precipitated silver oxide with hydrogen at a low temperature as Benton and Bell[1], and the electrolysed silver powder obtained by electrolysis of acidic silver nitrate solution as Titani et al.[2], were used and compared with each other.

Results

(a) The Experiments with the Reduced Silver Catalyst.

The results are shown in Fig. 1, where the amount of carbon dioxide produced for a minute,

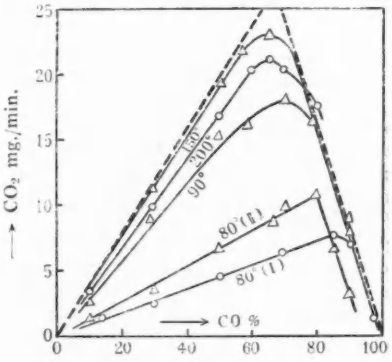

Fig. 1. Reaction rate with reduced silver catalyst.

the reaction rate, is plotted against mole percent of carbon monoxide in the mixed gas. The experiments were made at 80°, 200°, 150°, 90°, and again at 80°C. Benton and Bell[1] made their experiment in two limited composition ranges of the mixed gas, 0–20% and 90–100% of carbon monoxide. Now the reaction rate has been measured in the whole range of carbon monoxide-oxygen composition. The broken line in Fig. 1 shows the boundary, the maximum amount of carbon dioxide allowed for the composition of the mixed gas. Every curve in Fig. 1 increases with carbon monoxide content and falls at the boundary line. Comparing the curves 80° (I) and 80° (II), it is recognized that the catalyst has gradually increased its activity during the experiments. This may be due to the preliminary reduction with hydrogen before every run in order to avoid the deactivation of the catalyst by oxidation during the experiment. The data of the left hand part of every curve, which increases with carbon monoxide content in the

1) A.F. Benton and R.P. Bell, *J. Am. Chem. Soc.*, **56**. 501 (1934).

2) T. Titani and T. Ishiwatari, *J. Am. Chem. Soc.*, **65**, 13 (1944); T. Titani and N. Yamada, *ibid*, **65**, 224 (1944); T. Titani and S. Nakata, *ibid*, **65**, 305 (1944).

mixed gas, obey the following relation.

$$v=kP_{CO} \qquad (1)$$

where v is the reaction rate, number of mg. of carbon dioxide produced in one minute, k is the rate constant, and P_{CO} is the average partial pressure of carbon monoxide in the entering and exit mixed gas. Though the reaction rate in these experiment was larger than those of Benton and Bell[1], the kinetic relation (1) was qalitatively the same as theirs. That is, the reaction rate is proportional to the pressure of carbon monoxide and independent of the oxygen pressure.

(b) The Experiments with the Electrolysed Catalyst.

In the first experiment the electrolysed catalyst well-washed and dried was used without preliminary reduction with hydrogen. The results at

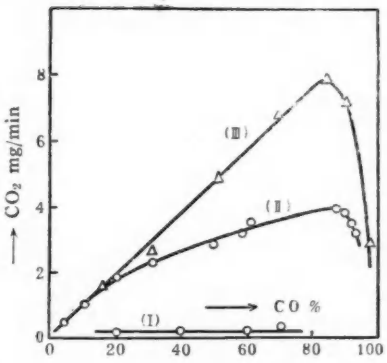

Fig. 2. Reaction rate with electrolysed silver catalyst at 80°C.

80°C are plotted as (I) in Fig. 2. The amount of carbon dioxide produced was very small. Then the catalyst was reduced in the hydrogen stream at 200°C for thirty minutes. The results of the second experiment after this treatment are plotted as (II) in Fig. 2. The catalyst was markedly activated and the reaction rate increased with the partial pressure of carbon monoxide. The data of the experiment with the reduced silver catalyst at 80°C, 80°(1) in Fig. 1, are plotted in Fig. 2 as (III) for comparison. It can be seen that by reduction with hydrogen the electrolysed catalyst was activated and approached to the reduced silver catalyst prepared from silver oxide.

(c) The Effect of Reduction and Poisoning with Hydrogen.

As mentioned above, it may be thought that when the surface of the silver catalyst has been fully reduced, the reaction rate increases with the partial pressure of carbon monoxide, the '*ascending*' type like the curve (II) and (III) in Fig. 2. If so, the surface of silver catalyst, which showed such low activity as (I) in Fig. 2 might have been oxidized or poisoned with oxygen. To make sure of this, the following experiment was made. The results are shown in Fig. 3. The electrolysed silver catalyst dried but not reduced preliminarily with hydrogen was used. The reaction rate was measured at 200°C in the first, the curve (I) in Fig. 3. The reaction rate decreased with carbon monoxide content in the mixed gas. The curve (I) in Fig. 3 is the '*descending*' type. This is the same type of curve as has been seen

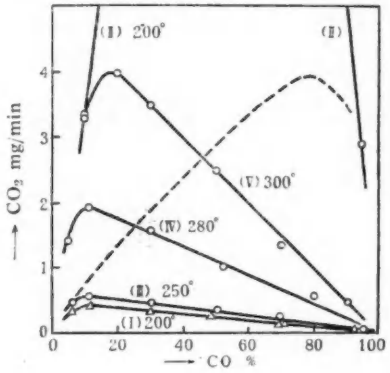

Fig. 3. Reaction rate with electrolysed silver catalyst and its changes by reduction and oxygenation.

in the experiment of Titani *et al*[2]. After the reduction of this catalyst in the hydrogen stream at 200°C, the reaction rate was measured again at 200°C. As was expected, the catalyst was remarkably activated, and the mixed gas reacted almost completely during the passage of the catalyt layer as was seen partially by (II) in Fig. 3. Then the catalyst was heated at 300°C in an oxygen stream for four hours, in order to poison the silver surface with oxygen. The results of three series of experiments at 250°, 280° and 300°C after this treatment are shown as (III), (IV), and (V) in Fig. 3. Clearly the catalyst was deactivated and the curves were of the '*descending*' type. The data on the straight line parts of these curves obey the following relation.

$$v=k'P_{O_2} \qquad (2)$$

where v is the reaction rate as the equation (1), k' is rate constant, and P_{O_2} is the average partial pressure of oxygen in the mixed gas. The reaction rate was proportional to the partial pressure of oxygen and independent of the carbon monoxide pressure. This was the case in the experiment of Titani *et al.*[2] For comparison with the curve (II) in Fig. 2, the results of the experiment at 80°C on the electrolysed silver catalyst reduced with hydrogen, is drawn into Fig. 3 as the broken line curve. It can be seen that the type of the curves is changed from '*ascending*' into '*descending*' type. The experiments by the use of the reduced silver catalyst from silver oxide was made also in a procedure similar to the above, and the same change by the treatment with oxygen could be seen.

Discussion

The results of the above experiments are

summarized and represented schematically in Fig. 4.

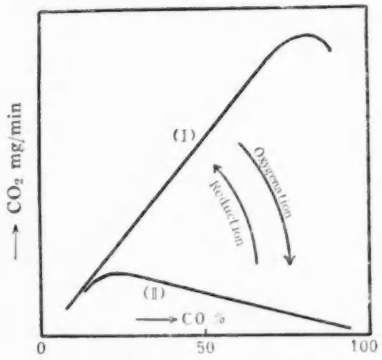

Fig. 4. Schematic representation of results.

When the surface of the silver powder has been fullly reduced with hydrogen, the rate of the catalytic oxidation of carbon monoxide on the surface describes the '*ascending*' type of reaction rate-composition curve as shown in Fig. 4 (I). The rate of reaction increases proportionally to the partial pressure of carbon monoxide and independently to the oxygen pressure. This is the case when the silver powder has been prepared by electrolysis of silver nitrate solution as well as by reduction of silver oxide. On the other hand, when the surface of silver powder has not been fully reduced or poisoned with oxygen, the catalyst is less active, and the reaction rate-composition curve is the '*descending*' type like (II) in Fig. 4. The reaction rate increases with the partial pressure of oxygen and is independent of the carbon monoxide pressure. This is the case when the catalyst is of the reduced silver from silver oxide as well as of the electrolysed silver. The 'ascending' type (I) in Fig. 4 corresponds to the result of the experiment of Benton and Bell[1], and the 'descending' type (II) corresponds to that of Titani et al[2]. One of these two different features of reaction rate dependency can be changed to the other by heating the surface of the silver catalyst in the stream of oxygen, or hydrogen.

These results indicate the following mechanism of oxidation of carbon monoxide on silver surface. This catalytic reaction consists mainly of the following two steps.

(i) $O_2 \longrightarrow 2O$ (chemisorption)

(ii) $O + CO \longrightarrow CO_2$

The step (i) is the chemisorption of oxygen on the surface of the silver catalyst. The oxygen molecules in the gas phase collide against the bare catalyst surface and are chemisorbed into atoms on it. In the next step (ii) the carbon monoxide molecules in the gas phase strike the chemisorbed oxygen on the surface of the silver catalyst and combine with them into carbon dioxide. If this is the mechanism of oxidation of carbon monoxide with silver catalyst, the following two limiting cases may occur.

(I) The case in which plenty of oxygen is chemisorbed on the catalyst surface.

In this case the amount of chemisorbed oxygen on a unit area of the surface of the silver catalyst must be large enough, and almost independent of the oxygen pressure. In consequence the reaction rate may be proportional to the rate of collision of carbon monoxide molecules on the catalyst surface, and accordingly to the partial pressure of carbon monoxide. That is,

$$v = kP_{CO}$$

This is the case when the silver powder prepared by the reduction of silver oxide with hydrogen is used, or generally when a silver catalyst has been treated with hydrogen and the catalyst surface has been fully reduced.

The activation energy for this case was calculated by the relation of the rate constant and the reaction temperature of the experiment (a) with the reduced silver catalyst.

$$A = 4.9 \text{ kcal.}$$

It may be presumed that the activation energy has the following content.

$$A = A_2 - Q/2$$

A_2 is the activation energy of the reaction step (ii), and Q is the heat of reaction step (i), or the heat of chemisorption of oxygen on the catalyst surface.

(II) The case in which only a little oxygen is chemisorbed on the catalyst surface.

In this case oxygen, as soon as it is chemisorbed on the catalyst surface, combines instantly with carbon monoxide. In consequence the total reaction rate is determined by the rate of chemisorption of oxygen on the catalyst surface. Accordingly it is proportional to the partial pressure of oxygen and independent of the carbon monoxide pressure, as following

$$v = k'P_{O_2}$$

This is the case when the electrolysed silver catalyst not reduced is used, or generally when a silver catalyst has been treated with oxygen and poisoned the surface.

The activation energy was calculated from the data of the experiments (III), (IV), and (V) in Fig. 3.

$$A' = 23.6 \text{ kcal.}$$

This activation energy A' must be the activation energy A_1 of the reaction step (i), or of chemisorption of oxygen on this poisoned catalyst surface.

$$A' = A_1$$

Thus, it can be explained by the above consideration that the different features of the reaction appear with reduction or oxydation of a catalyst surface. It my be concluded that Benton and Bell measured the reaction rate on the fully reduced silver surface, and that Titani et al. on the surface poisoned with oxygen. The difference between the two is by no means contradictory.

Summary

The catalytic oxidation of carbon monoxide on the surface of silver powder has been studied. The reaction rate has been measured by the flow method. The reaction rate on the fully reduced silver surface is proportional to the pressure of carbon monoxide and independent of the oxygen pressure. On the other hand, when the surface has not been reduced with hydrogen, or has been treated preliminarily in an oxygen stream at a high temperature, the reaction rate is proportional to the oxygen pressure and independent of the carbon monoxide pressure. One of these two features of the reaction can be changed to the other by heating the surface in the stream of oxygen, or hydrogen. These results indicate that the chemisorption of oxygen and the reaction between this chemisorbed oxygen and carbon monoxide are the main steps of the oxidation, and its reaction rate is determined by either of these steps.

The author wishes to express his cordial thanks to Dr. T. Titani, Professor of Tokyo Metropolitan University, for helpful discussion and encouragement.

Faculty of Liberal Arts and Science, Toyama University

Sterols and Other Unsaponifiable Substances in the Lipids of Shell Fishes, Crustacea and Echinoderms. XIII. Sterol Components of Star Fish, Luidia quinaria von Martens

By Yoshiyuki TOYAMA and Toru TAKAGI

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Among the sterol components of star fish, stellasterol ($C_{27}H_{44}O$, m.p. 149~150°, m.p. of its acetate 176~177°)[1] in *Astropecten aurantiacus* and asteriasterol (m.p. 70°)[2] in *Asterias forbesi* were known in earlier times. Later studies,[3] however, revealed that asteriasterol, like astrol[4] in *Astropecten aurantiacus*, is identical with batyl alcohol. Bergmann and Stansbury[5] separated a sterol fraction resembling stellasterol from *Asterias forbesi*, but they found that this fraction is not a single sterol but a mixture of two sterols, $C_{28}H_{46}O$ (F_2) and $C_{28}H_{48}O$ (F_1). Although neither components were separated from each other, both components were shown to have an ethylenic linkage at C-8, the di-unsaturated component having one more ethylenic linkage at the 22 : 23-position. These authors retained the name stellasterol for the di-unsaturated $C_{28}H_{46}O$, and designated the mono-unsaturated $C_{28}H_{48}O$ as stellastenol. According to Barton,[9] who examined the relations between the optical activities of these sterols and their esters, the ethylenic linkage common to stellasterol and stellastenol is located at the 7 : 8-position. One of the present authors, Toyama, and Matsumoto[7] separated hitodesterol (m.p. 167~168°, m.p. of its acetate 181~182°) from *Asterina pectinifera* (Müller et Troschel). Although the formula $C_{28}H_{42}O$ or $C_{29}H_{44}O$ was given for hitodesterol at that time, this formula has been found to be erroneous by later investigation in our laboratory[8] and hitodesterol was assumed now to have the formula $C_{28}H_{46}O$ or $C_{29}H_{48}O$, having a close resemblance to stellasterol, chondrillasterol, and spinasterol, possibly identical with one of them. Meanwhile, the occurrence

1) A. Kossel and S. Edelbacher, *Z. Physiol. Chem.*, **94**, 264 (1915).
2) J.H. Page, *J. Biol. Chem.*, **57**, 471 (1923).
3) l. c., (*J*).
4) T. Matsumoto, M. Yajima and Y. Toyama, *J. Chem. Soc. Japan*, **64**, 1203 (1943); W. Bergmann and H. A. Stansbury, Jb., *J. Org. Chem.*, **8**, 283 (1943).
5) W. Bergmann and H.A. Stansbury, Jb., *J. Org. Chem.*, **9**, 281 (1944).
6) Cf. L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene" 1949, p. 297.
7) T. Matsumoto and Y. Toyama, *J. Chem. Soc. Japan*, **64**, 1069 (1943).
8) Y. Toyama, not yet published.

of another sterol (m.p. 144~146°, m.p. of its acetate 160~162°) in *Asterina pectinifera* (*Patiria pectinifera*) was reported by Kuwata and Ban.[9] This sterol, named patiriasterol, was concluded to be identical with $\Delta^{22:23}$-ergostenol by these authors.

In this paper, the results of our studies on the sterol components of star fish, *Luidia quinaria* von Martens, are recorded. The sterol mixture, as a whole, consisted chiefly of mono-unsaturated sterol. The acetate of the sterol mixture was subjected to fractional crystallization, yielding several acetate fractions which had somewhat different iodine values by the perbenzoic acid method. The acetate fraction of higher melting point showed a higher iodine value than the acetate fraction higher iodine value than the acetate fraction of lower melting point, indicating the presence of a lesser amount of saturated and di-unsaturated sterols in addition to mono-unsaturated sterol in the original sterol mixture. By repeated fractional crystallizations of the acetate mixture, two sterol fractions I (m.p. 145~147°, m.p. of its acetate 157°) and II (m.p. 135°, m.p. of its acetate 149°) were obtained. Both fractions consisted of mono-unsaturated sterol. The acetates of the fractions I and II absorbed no hydrogen in the presence of palladium black in glacial acetic acid, but they underwent isomerization, as is the case with a $\Delta^{7:8}$-sterol. Bromination-debromination of the acetate of the fraction I resulted in the formation of 7:8, 9:11-conjugation which presented a further evidence for the presence of 7:8-ethylenic linkage in the fraction I.[10] Although the fraction II might consist of another $\Delta^{7:8}$-sterol which is different from the $\Delta^{7:8}$-sterol of the fraction I, it is also possible that both fractions consist of the same $\Delta^{7:8}$-sterol and differ only in their purity. Comparing the fraction I and patiriasterol, the melting points of free sterols and their corresponding esters are fairly close to each other, but they differ decisively in their behavior toward hydrogenation. While patiriasterol has its ethylenic linkage at the 22:23-position, the ethylenic linkage of the fraction I is located convincibly at the 7:8-position. On the other hand, the fraction I agrees with stellastenol in the position of ethylenic linkage, both having 7:8-ethylenic linkage, but it is not yet decided whether the sterol in the fraction I is C_{28}-sterol or C_{29}-sterol. For the sake of comparison, the properties of γ-spinastenol (C_{29}), $\Delta^{7:8}$-ergostenol, patiriasterol, and the sterol fractions I and II, together with some derivatives of the respective sterols are shown in Table I.

TABLE I

	Free sterol		Acetate		Benzoate		α-Isomer		Acetate of α-isomer	
	m.p., °C	$[\alpha]_D^\circ$	m.p., °C	$[\alpha]_D^\circ$	m.p., °C	$[\alpha]_D^\circ$	m.p., °C	$[\alpha]_D^\circ$	m.p., °C	$[\alpha]_D^\circ$
γ-Spinastenol (11)	144–145	+11	156–157	+8	180.5	+13	112–113	+23	116–117	+12
$\Delta^{7:8}$-Ergostenol (12)	148	−2	157–159	+4	180.5	+2	132	+11	109	0
Patiriasterol	144–146	+4.4	160–162	+4.2	175–176	+7.1	—	—	—	—
Sterol fract. I	145–147	+9	157	+6	177	—	115	—	111–112	+18
Sterol fract. II	135	+2	149	+2	171	—	114	—	115	+8

Experimental

A lot of star fish, *Luidia quinaria* von Martens, caught around the Osaki-Shimojima Island in the Inland Sea of Seto in August, 1952, were sun-dried. The dried material (1,030 g.) was cut into small pieces and then extracted with ether, yielding 29 g. (2.8%) of ether extract which was a viscous liquid of reddish orange color and deposited a large amount of solid in the winter season. On treating the ethereal extract with 300 cc. of acetone, 22.1 g. of acetone-soluble portion (fat) and 6.9 g. of acetone-insoluble portion (phosphatide) were separated. The acetone-soluble portion was a reddish orange oil having the following characteristics: d_4^{20} 0.9405, n_D^{20} 1.4740, acid value 111.8, saponification value 143.9, iodine value by the Wijs method 132.4, unsaponifiable matter 28.16%.

The acetone-insoluble portion gave only 0.3 g. of unsaponifiable matter by extraction of the saponified product with ether. The unsaponifiable matter (6 g.) obtained from the acetone-soluble

9) S. Kuwata and Shoichi Ban, *J. Pharm. Soc. Japan*, **69**, 212 (1949).

10) Cf. R. C. Anderson, R. Stevenson and F. S. Spring, *J. Chem. Soc.*, **1952**, 2901.

11) D. H. R. Barton and J. D. Cox, *J. Chem. Soc.*, **1948**, 783.

12) D. H. R. Barton and J. D. Cox, *J. Chem. Soc.*, **1948**, 1354.

portion was recrystallized twice from methanol, yielding 2.2 g. of crude sterol, which had m.p. 125~129°, iodine values 65.6 by the perbenzoic acid method and 177.4 by the pyridine sulfate dibromide method. The ultraviolet absorption spectra of the crude sterol indicated the absence of provitamin D. The steryl acetate (2.0 g.) prepared by acetylation of crude sterol had m.p. 135~141° and saponification value 127.1. This was subjected to repeated recrystallizations as shown in Table II.

TABLE II

No. of recrystallization	Solvent	Acetate, crystallized out		Acetate, recovered from mother liquor	
		Yield g.	m.p. °C.	m.p. °C.	Iodine v. by the perbenzoic acid method
1	Methanol	1.9	143–144	104–106	43.4
2	Ethanol	1.6	146–148	105–110	—
3	"	1.1	147–152	124–126	—
4	Acetone	0.5	156–159	147–149	—
5	"	0.25	156–159	147–149	62.6
6	"	0.10	162–165	157–159	70.7
7	"	0.08	162–165		
8	"	0.02	174–175	165–166	—

Iodine values, calculated: $C_{30}H_{50}O_2$ (F_1) 57.3, $C_{31}H_{52}O_2$ (F_1) 55.6

Sterol Fraction I. The acetate of m.p. 157–159°, recovered from the mother liquor of recrystallization in Table II, was fractionally crystallized from acetone, yielding 1st crop of m.p. 160°, 2nd crop of m.p. 157° and 3rd crop of m.p. 152°. The 2nd crop showed no change in its melting point by further recrystallizations from acetone and ethanol-ether and the final product had saponification value 124.9 (calculated, $C_{30}H_{50}O_2$ 126.7, $C_{31}H_{52}O_2$ 122.8), iodine values 63.5 by the perbenzoic acid method 190.1 by the pyridine sulfate dibromide method, and $[\alpha]_D^{10}$+5.6°. The free sterol obtained by saponification of the acetate had, after recrystallization from methanol, m.p. 145–147° and $[\alpha]_D^{10}$+9.0°. Benzoylation of the free sterol gave a benzoate of m.p. 177°.

A solution of the acetate of m.p. 152° with a palladium black catalyst in glacial acetic acid was shaken under the atmosphere of hydrogen for 3 hours at room temperature. Absorption of hydrogen did not occur at all, but the acetate underwent isomerization during this treatment, forming an isomer (α-isomer) which showed, after recrystallization from methanol, m.p. 111–112° and $[\alpha]_D^{25}$+18.1°. The free sterol obtained by saponification of this acetate melted at 115°.

The acetate (0.05 g.) of m.p. 152° was dissolved in 10 cc. of ether, and 5 cc. of a 2% solution of bromine in ether was added dropwise. After standing for one hour, a mixture of 0.25 g. of potassium iodide dissolved in a small amount of water and 10 cc. of ethanol was added to the solution of brominated product, and the mixture was allowed to stand for 48 hours in order to complete debromination. An aqueous solution of sodium bisulfite was then added, and the mixture was extracted with ether. The ethereal extract, after recrystallization from methanol, melted at 164° and exhibited the characteristic ultraviolet absorption spectra of 7:8, 9:11-conjugated sterol; $\log \varepsilon_{235}$ 3.91, $\log \varepsilon_{242}$ 3.88, $\log \varepsilon_{251}$ 3.80.

Sterol Fraction II. The acetate of m.p. 147~149°, recovered from mother liquors of recrystallization in Table II, was fractionally crystallized from acetone. After removing higher and lower melting fractions, a fraction of m.p. 148~149° was separated and further recrystallized from acetone, ethanol-ether and methanol-acetone until an acetate of a constant melting point of 149° was obtained. It had saponification value 123.4, iodine values 60.1 by the perbenzoic acid method and 170.9 by the pyridine sulfate dibromide method, and $[\alpha]_D^{12}$+2.2°. Saponification of the acetate gave a free sterol of m.p. 135° and $[\alpha]_D^{12}$+1.6°. Benzoylation of the free sterol gave a benzoate of m.p. 171°.

On shaking a solution of acetate of m.p. 149° with a palladium black catalyst in glacial acetic acid under the atmosphere of hydrogen for 3 hours, isomerization without absorption of hydrogen occurred, yielding an isomerized product (α-isomer) of m.p. 115° and $[\alpha]_D^{25}$+7.9°. Saponification of this product gave a free sterol of m.p. 114°.

Summary

Sterol mixture of star fish, *Luidia quinaria* von Martens, has been found to consist largely of mono-unsaturated sterol with a lesser amount of saturated and di-unsaturated sterols. By fractional crystallization of steryl acetate mixture, sterol fractions I (m.p. 145° and m.p. of its acetate 157°) and II (m.p. 135° and m.p. of its acetate 149°) were separated. Both fractions were found to consist of $\Delta^{7:8}$-sterol of C_{28} or C_{29} series. It requires some further research to decide whether each fraction consists of a different individual sterol or both fractions consist substantially of the same sterol, differing only in their purity.

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Enzymatic Reduction of Aromatic Nitro, Nitroso and Hydroxyl amino Compounds

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In the previous paper[1], the nature of the enzyme system participating in the reduction of aromatic nitro-compounds was described.

This paper describes the route of the enzymatic reduction of nitro-compounds to amino-compounds. It is well known that when aromatic nitro-compounds such as trinitrotoluene or dinitrophenol are administrated to animals, the corresponding amino, hydroxylamino, and azoxy compounds are excreted in the urine[2][3]. These products are considered as intermediate or by-products in the biological reduction of nitro-compounds to amino-compounds[4][5][6][7][8]. Concerning the route of the reduction, we assumed at first the following successive reduction of the nitro to the amino, taking into consideration that biological oxido-reductions generally take place by the two-electron steps:

Nitro→Nitroso→Hydroxylamino→Amino

However, we paid attention also to such substances as azoxy, azo, and hydrazo compounds, which are known to be intermediates in organo-chemical reduction of aromatic nitro-compounds.

Experimental Methods

We used as substrates nitroso[9], hydroxylamino[9], azoxy[10], azo[11], and hydrazo[12] compounds in the series of *o*-benzoic acid, because they are all sufficiently water-soluble and stable for the enzymatic study. The preparation of the enzymes from a halotolerant bacterium, the experimental conditions, and the methods of estimation of the reaction velocity were the same as for those described in the preceding report.

1) I. Yamashina, This Bulletin in the press.
2) R.T. Willhams, G.T. Mills and H.J. Channon, *Biochem. J.*, **38**, 72 (1944).
3) H. Mayer, A. Mayer and L. Plantefol, *Ann. physiol. physicochem. biol.*, **8**, 1 (1932).
4) G.D. Greville and K.G. Stern, *Biochem. J.*, **29**, 487 (1949).
5) H.G. Bray, W.V. Thorpe and P.B. Wood, *Biochem. J.*, **44**, 39 (1949).
6) D. Robinson, J.N. Smith and R.T. Williams, *Biochem. J.*, **48**, xxvii (1951).
7) H.G. Bray, R.C. Clowes and W.V. Thorpe, *Biochem. J.*, **49**, lxv (1951).
8) H.G. Bray, Z. Hyhs and W.V. Thorpe, *Biochem, J.*, **49**, xcv (1651).
9) E. Bamberger and F.L. Pyman. *Ber.*, **42**, 2307 (1909).
10) G. Heller, *Ber.*, **41**, 2690 (1908).
11) J. Maier, *Ber.*, **34**, 4135 (1901).
12) R. Loewenherz, *Ber.* **25**, 2797 (1892).

Results and Discussion

Enzymatic Reduction of *o*-Nitroso- and *o*-Hydroxylamino Benzoic Acid:

The measurements of the reaction velocity were carried out by the determination of the anthranilic acid produced. As shown in Fig. 1 and Fig. 2, they were reduced enzymatically by the hydrogen donator system such as the

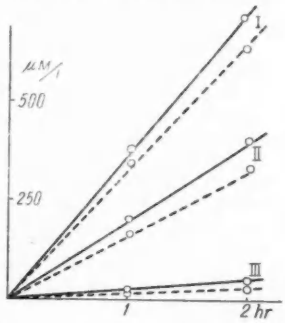


Fig. 1. The formation of anthranilic acid from *o*-nitroso, *o*-hydroxylamino benzoic acids in the presence of hydrogen carriers, -○- nitroso, - - ○ - - hydroxylamino. System: Substrate (6×10^{-3}M) 1 cc., Reductase 1 cc., H. Carrier (10^{-3}M) 0.4 cc., Dehydrogenase (5 mg./cc.) 1 cc., Buffer (pH 6.8, 10^{-1}M, phosphate) 1 cc., HCOONa (10^{-1}M) 1 cc., H_2O 1.6 cc., I: Nile Blue, II: Methylene Blue, III: no carrier.

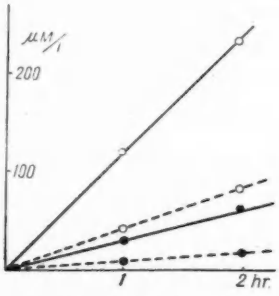


Fig. 2. The formation of anthranilic acid with leuco M.B. as hydrogen donator, -○- nitroso, -○- hydroxylamino, ----- no enzyme.
System: Substrate (6×10^{-3}M) 1 cc., Leuco M.B. (10^{-2}M) 2 cc., Buffer 1 cc., Reductase 1 cc..

system consisting of hydrogen donator, dehydrogenase and an appropriate intermediary hydrogen carrier or by the leuco-form of appropriate redox dyes.

It is noteworthy that methylene blue is effective as a hydrogen carrier in these cases, contrary to the case of the reduction of the nitro group. From these results it may be concluded that the water-extract of the freeze-dried cells of the halotolerant bacterium contains the enzymes which accelerate the reduction of aromatic nitroso and hydroxylamino groups. We should like to call them "nitroso-reductase" and "hydroxylamino-reductase" respectively. The effects of various inhibitors on nitroso- and hydroxylamino- reductases are shown in Tab. I. The inhibiting action of cyanide and azide are so strong that the participation of some heavy metal to the enzyme reaction may be supposed. The inhibition is even greater than that on nitro-reductase.

Table I

The Effects of Several Inhibitors

	Nitroso	Hydroxylamino
KCN 10^{-3} M	80%	70%
NaN_3 10^{-2} M	40	30
NaF 10^{-2} M	10	10
Mn^{++} 10^{-4} M	—	0

As shown in Fig. 1 and Fig. 2, the velocity* of the enzymatic reduction of nitro is larger than that of hydroxylamino. It is not due to the inhibition by the excess of substrate in the latter case, because the velocity of the formation of amino from hydroxylamino is quite proportional to the concentration of the substrate (Fig. 3).

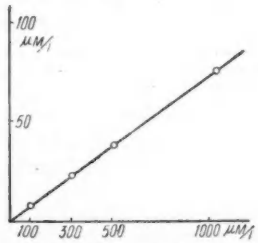


Fig. 3. The relation of the formation of anthranilic acid and the conc. of substrate (*o*-hydroxylamino benzoic acid.
System: Substrate 1 cc., Reductase 1 cc., Leuco M.B. (10^{-2}M) 2 cc. Buffer 1 cc.
Time: 2 hr.

These facts suggest that the hydroxylamino compound may not be a normal intermediate in the enzymatic reduction of nitroso compounds.

Experiments with *o, o'*-Azoxy, *o, o'*-Azo, and *o, o'*-Hydrazo Benzoic Acids:

They were not reduced in the presence of our enzyme preparation by the hydrogen donator-dehydrogenase system (nile blue or methylene blue as hydrogen carriers) nor by leuco methylene blue. So these substances can be excluded from the possible intermediates of the reduction from the nitro compound to the amino compound. However *o, o'*-azoxy benzoic acid was formed as a by-product in the reduction of *o*-nitrobenzoic acid as will be shown later (Fig. 5).

Route of the Enzymatic Reduction:

As the velocity of the enzymatic formation of amino group from nitroso group is larger than that from hydroxylamino group as mentioned above, the main route of nitroso to amino cannot be

nitroso→hydroxylamino→amino,

but it must be

nitroso→X→amino
nitroso→amino.

As azoxy, azo and hydrazo compounds, which had been supposed to be X in the reaction scheme, were not reduced enzymatically, we have been led to the conclusion that the direct four-electron reduction from nitroso to amino may be the main route of the enzymatic reduction.

In order to further ascertain the conclusion, we tried to detect the intermediates and the by-products of the enzymatic reaction by paper-chromatography. The reaction mixture (Each of the above-mentioned compounds and dehydrogenase system) was extracted with other, dried in the refrigerator and the residue was dissolved in a small quantity of ether and tested by paper chromatography. The composition of the developing solvents and *Rf* values of various compounds are shown in Tab. II.

Table II. The Developing Solvents and *Rf* Values

Solvents; (1)

Ethanol	40%	Butanol	33%
Butanol	20	Pyridine	33
Ammonia (s.g.=0.90)	20	sat. NaCl aq.	33
Benzene	20	The organic layer of above mixture	

(2) *Rf* Values:

Benzoic acids	Solvent (1)	Solvent (2)
o-nitro	0.63	0.68
o-amino	0.51	0.91
o-nitroso	0.20	0.30
o-hydroxyl-amino	0 02	—
o, o'-azoxy	0.24	0.65
o, o'-azo	0.28	—
o, o'-hydrazo	0.33	—

*) Measured by the formation of amino group.

For the detection of each spots, Ehrlich's reaction for amino compounds was carried out directly or after the reduction by $SnCl_2$-HCl. Axoxy, azo and hydrazo compounds appeared as red spots and others as yellow spots.

The enzymatic reduction of nitroso was followed by paper chromatography as shown in Fig. 4. At the first stage of the reaction the spot of hydroxylamino appeared intensely; it then gradually became feeble and afterwards disappeared. From these results it must be considered that besides the direct route there is also a route by which the nitroso is reduced enzymatically to amino via hydroxylamino.

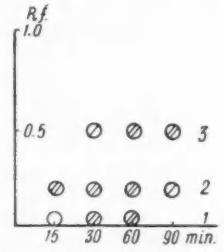


Fig. 4. Solvent (1) (Table II)
1: *o*-hydroxylamino benzoic acid
2: *o*-nitroso " "
3: *o*-amino " "

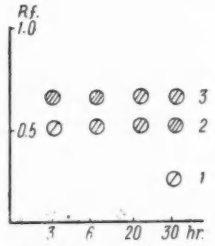


Fig. 5. Solvent (1) (Table II)
1: *o,o'*-azoxy benzoic acid
2: *o*-amino " "
3: *o*-nitro " "

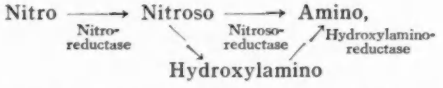
On the paper chromatogram of the reduction products of the nitro to the amino, as shown in Fig. 5, the spot of azoxy compound was detected, besides the spots of decreasing nitro and of increasing amino. Taking into consideration the fact that the azoxy compound cannot be reduced by our enzyme preparation, it must be regarded as a by-product. The reason why any substance other than nitro, amino and azoxy benzoic acids was not detected may be explained by assuming that the possible intermediates, nitroso and hydroxylamino benzoic acids, are so rapidly reduced that they do not accumulate appreciably. This consideration is also supported by the fact that the quantity of the amino compound formed was equivalent to that of the nitro compound reduced, which in turn was estimated by the polarography.

TABLE III.

	0 hr.	9 hr.	Degree of diminution or formation
nitro	100%	68%	32%
amino	0	33	33
nitro	100	76	20
(in the presence of 10^{-3} M KCN)			(degree of inhibition is 25%)

Moreover, the paper chromatography disclosed the existence of the nitroso compound as a reduction product in the enzymatic reduction of the nitro compound under the presence of 10^{-3} M KCN. In this condition, the enzymatic formation of amino from nitro was reduced to 30%, that from nitroso to 20% and that from hydroxylamino to 30%, while the rate of the enzymatic reduction of nitro measured by polarography was reduced only to 75%. These facts are easily explained by considering the that primary product of the enzymatic reduction of the nitro compound is the nitroso compound and that this stage of successive reduction is less inhibited by KCN than the latter stages.

All of the results concerning the reduction process of nitro to amino may be summarized as follows:



although it must be mentioned that we have as yet not been able to obtain experimental evidence that nitroso-reductase and hydroxylamino-reductase are different. The accumulation of azoxy compound, a by-product, is probably due to the condensation of nitroso and hydroxylamino compound.

Summary

1) A cell-free enzyme preparation of a halotolerant bacterium activates aromatic nitroso and hydroxylamino compounds as well as nitro compounds and accelerates their reduction by hydrogen donator systems.
2) The enzymatic reduction of nitroso and hydroxylamino was more strongly inhibited by cyanide and azide than that of nitro.
3) Methylene blue, which can not be used as an intermediary hydrogen carrier in the case of nitro reduction, can be used in the

cases of nitroso and hydroxylamino reduction.

4) From these facts, we have been led to the consideration that there exist special enzymes such as nitroso-reductase and hydroxylamino-reductase besides nitro-reductase.

5) Azoxy, azo, and hydrazo compound cannot be reduced by the enzyme preparation.

6) From the studies of reaction velocity and paper chromatography of the intermediates and the end products, we proposed a scheme concerning the enzymatic reduction of nitro to amino, namely:

$$\text{Nitro} \rightarrow \text{Nitroso} \rightarrow \text{Amino}$$
$$\searrow \quad \nearrow$$
$$\text{Hydroxylamino}$$

The expenses of this study were defrayed in part by a grant from Japanase Biological Research Works, Ltd. and Seikagaku-Kenkyujo Ltd., to both of which the authors' thanks are due.

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Isopropoxypolysiloxanes

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The preparation of tetraisopropoxysilane from silicon tetrachloride and isopropanol was attempted in vain by Dearing[1]. Recently Bradley and his co-workers[2] reported briefly its formation from the same materials. We wish now to report on the preparation and properties of tetraisopropoxysilane $((CH_3)_2CHO)_4Si$ (I), hexaisopropoxydisiloxane $((CH_3)_2CHO)_3SiOSi((CH_3)_2CHO)_3$ (II), and octaisopropoxytrisiloxane $((CH_3)_2CHO)_3SiOSi((CH_3)_2CHO)_2OSi((CH_3)_2CHO)_3$ (III).

For the starting material isopropanol of Shell Chemicals (b.p. 82.2°C, n_D^{20} 1.3776) was used without further purification. For the preparation of (I) and (II) redistilled silicon tetrachloride (b.p. 57–58°C), and for the preparation of (III) octachlorotrisiloxane $Cl_3SiOSiCl_2OSiCl_3$ were used. This substance was obtained from the distillation residue of industrial silicon tetrachloride with rigorous fractionation through the helices packed column of about 20 plates under reduced pressure. (b.p. 73°C./13 mm., Anal. Calcd. for $Cl_8Si_3O_2$: Cl, 70.9. Found: Cl, 70.8.)

Preparation of Tetraisopropoxysilane (I) and Hexaisopropoxydisiloxane (II):—In the 1 *l.* three-necked flask equipped with an efficient stirrer, dropping funnel and reflux condenser, isopropanol (240 g., 4 mol.) was placed. Redistilled silicon tetrachloride (170 g., 1 mol.) was added with vigorous stirring for 2 hours. During the addition, the mixture was kept under 5°C. After addition the temperature was gradually raised to 40°C. for an hour and kept at this temperature for additional 3.5 hours. The mixture amounted to 360 g. (Cl content 62%). At this temperature, the mixture was dehydrochlorinated by bubbling dry air through the mixture until the chlorine content of the mixture became constant, the final value was 0.2% after 7 hours aeration. The volume of air passed was 400 *l.* At this stage the weight of the mixture amounted to 245g. (Yield: 91% theory). Hydrated sodium carbonate (5 g.), containing about 2 moles H_2O to Na_2CO_3, was added and the mix.

TABLE ISOPROPOXYPOLYSILOXANES

Name	Formula	Boiling Point °C./mm.	Refractive Index n_D^{20} n_D^{30}	Density d_4^{20} d_4^{30}	Molar Refraction Found (Calcd.)**	Molecular Weight Found*** (Calcd.)	% Si Found (Calcd.)
Tetraisopropoxysilane	$[(CH_3)_2CHO]_4Si$ (I)	93–4/28*	1.3835 1.3787	0.8744 0.8656	70.7 (70.4)	267 (265)	10.59 (10.62)
Hexaisopropoxydisiloxane	$[(CH_3)_2CHO]_3Si_2O$ (II)	82–3/2	1.3921 1.3875	0.9236 0.9150	110.1 (109.0)	420 (427)	13.14 (13.17)
Octaisopropoxytrisiloxane	$[(CH_3)_2CHO]_8Si_3O_2$ (III)	121–2/2	1.3960 1.3912	0.9504 0.9419	148.9 (147.7)	585 (589)	14.37 (14.31)

* 74°C/13 mm., 116°C./85 mm. Bradley, *et. al., loc. cit.*

** Calculated from bond refrativities by E. L. Warrick, *J. Am. Chem. Soc.* **68**, 2455 (1946)

*** Cryoscopic measurements in benzene

1) A.W. Dearing and E.E. Reid, *J. Am. Chem. Soc.*, **50**, 3058 (1928).

2) D.C. Bradley, R.C. Mehrotra and W. Wardlaw. *J. Chem. Soc.*, **1952**, 5020.

ture was warmed to 80°C. with shaking. The filtrate (240 g.) was distilled under reduced pressure by a Claisen flask, and the fraction boiling at 90°–95°C./30 mm. was collected. (Crude (I), 230g., Yield: 85% theory) This fraction and the residue of several runs, from which the (II) was obtained, were fractionated rigorously by a Stedman column of about 20 plates respectively. The properties of these fractions are summarized in the following Table.

If the treatment of hydrated sodium carbonate was not carried out, the distillate obtained after several fractionations usually still contained a trace of isopropoxychlorosilane which fumes in moist air. After the treatment with an excess of hydrated sodium carbonate equivalent to convert Si–Cl to Si–O–Si no trace of fuming compound was found in the filtrate. Furthermore the decomposition of the isopropoxysilane was not observed even after prolonged heating at about 80°C.

Preparation of Octaisopropoxytrisiloxane (III):—In the 300 cc. three-necked flask equipped as above, was placed octachlorotrisiloxane. (40 g., 0.1 mol.) Isopropanol (48 g., 0.8 mol.) was added with vigorous stirring for 1.5 hours. During the addition, the temperature of the mixture was kept under5 °C. after which the temperature was gradually raised to 40°C. for 0.5 hour and kept at this temperature for additional one hour. The weight of the mixture amounted to 60 g. This mixture was aerated at this temperature until the chlorine content became constant. The volume of air passed was 280 *l* during a course of 8 hours and the final chlorine content was 1.2%. (Yield: 55 g., 94.8% theory) To this was added hydrated sodium carbonate (7 g.) and treated as above. The filtrate (51 g.) was rigorously fractionated by the Stedman column. About 5 g. of low boiling fraction (80°–110°C./2 mm.) was obtained. Judging from the boiling point, this may be considered to be hexaisopropoxydisiloxane (II) produced by a fission of siloxane chain, but was not further examined. The properties of constant boiling fraction (III) are given in the Table together with (I) and (II).

The authors wish to express their sincere thanks to Dr. Watase for his gracious encouragement during this work. Our thanks are also due to the Ministry of Education for a grant in aid of this research.

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Chemical Studies On Ion Emission from Solids. II. A Method of Micro-Determination of An Alkali Salt in Aqueous Solution by Measuring Positive-Ion Emission

By Nobuji SASAKI and Toshiyoshi YUASA

(Received May 28, 1953)

Commercial alumina-coated tungsten filament operating as a heater in a vacuum tube, emits positive ions at about 800°C. They consist of sodium and potassium ions, as shown mass-spectrographically by H. Inoue[1] in our laboratory. The emission decays[2] with respect to time nearly exponentially. To the filament thus freed from alkalis by long heating was mounted* a known amount (about one mg.) of aqueous sodium chloride solutions in various ranges of concentration. The total number of positive ions emitted from the filament by heating was measured and plotted against the concentration of sodium. The resulting smooth curve may be used for determining the extremely low concentration of sodium, only one milligram of sample solution (e.g. a rain drop) being required.

Experimental

A piece of alumina-coated tungsten filament, 60 mm. in length and 0.051 mm. in diameter, was mounted as anode along the axis of a cylindrical cathode of 15 mm. diameter by screw-binders for convenient dismounting. The ions reaching to the cathode were measured by a galvanometer (1.1×10^{-11} amp./mm.) under the following conditions—applied voltage being 60 V., temperature of the filament about 750°C, pressure about 10^{-5} mm.Hg. Further details of the apparatus were explained in the previous report.[2] For preparing sample solutions only quartz apparatus was used to avoid any contamination of alkalis.

Determination of the Total Number of Positive Ions Emitted.—Aqueous sodium chloride solutions of various ranges of known concentration were prepared as standard using distilled water. Reading of the galvanometer was taken fifteen seconds after the heating current of filament was switched in. The current-time curves

1) The results were read at the Meeting of the Chemical Society of Japan (Kinki-Branch), Oct., 1949.

2) N. Sasaki and T. Yuasa, *J. Chem. Soc. Japan*, **73**, 273 (1952).

* The weight of a small amount of a volatile liquid such as the sample solution mounted to the filament was determined by a method to be described elsewhere.

of some representative results (No (3), (5), (7), (12), (14)) are shown in Fig. 1. The total number of

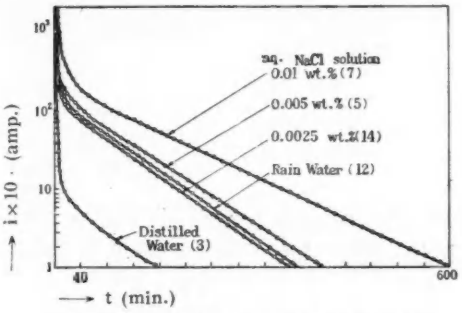

Fig. 1.—Emission Current-time curve

positive ions for each solution was obtained by integrating the emission currents with respect to ime (Table I). They give a smooth curve when plotted against the concentration (Fig. 2).

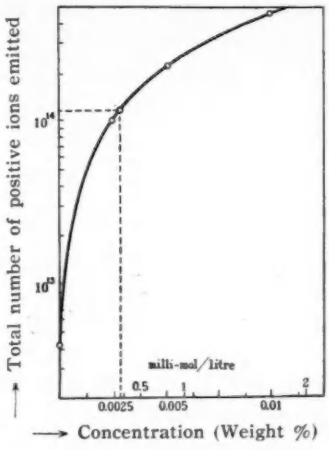

Fig. 2.—Total number of positive ions VS. Concentration curve

TABLE I

Samples	Order of measurement	Weights of the samples applied (W) in mg.	Total number of positive ions emitted (N)	N/W	Means
NaCl aq. soln.	(7)	0.864	3.70×10^{14}	4.28×10^{14}	
0.01 wt. %	(8)	1.093	4.77×10^{14}	4.36×10^{14}	4.29×10^{14}
	(9)	0.870	3.70×10^{14}	4.25×10^{14}	
	(4)	1.016	2.00×10^{14}	1.96×10^{14}	
0.005 wt. %	(5)	0.907	1.86×10^{14}	2.05×10^{14}	2.05×10^{14}
	(6)	0.851	1.82×10^{14}	2.13×10^{14}	
	(13)	0.901	8.41×10^{13}	0.93×10^{14}	
0.0025 wt. %	(14)	1.078	1.10×10^{14}	1.02×10^{14}	1.01×10^{14}
	(15)	0.924	9.98×10^{13}	1.08×10^{14}	
	(1)	0.909	3.75×10^{12}	4.12×10^{12}	
Distilled Water	(2)	1.091	4.64×10^{12}	4.25×10^{12}	4.19×10^{12}
	(3)	1.007	4.23×10^{12}	4.20×10^{12}	
	(10)	1.005	4.23×10^{12}	4.20×10^{12}	
Rain Water	(11)	1.013	1.17×10^{14}	1.15×10^{14}	1.13×10^{14}
	(12)	1.062	1.18×10^{14}	1.11×10^{14}	

The total number of positive ions emitted from one mg. of distilled water is nearly equal to the probable errors of N/W of aqueous sodium chloride solutions of various ranges of concentration, so that no correction was made for the blank value of distilled water.

The ratios of N/W to N_0, the total number of sodium ions contained in one mg. of solutions, are strikingly constant for wide ranges of concentration, namely, 0.38, 0.39 and 0.41 respectively for 0.0025, 0.005 and 0.01 weight per cent aqueous sodium chloride solutions. The rest of sodium ions seem to have evaporated as neutral molecules or atoms.

Similar measurements were made with aqueous potassium chloride solutions and a calibration curve of the same type was obtained.

Ionic emission from mixed KCl–NaCl solutions have been found greater than those calculated by the additive law. Ionic emission from more complicated mixtures was investigated by H. A. Barton and coworkers[3], and B. Toubes and coworker[4], finding that only alkali metal ions were emitted at about 800°–1000°C from the mixture of alkali and alkaline earth salts, while the alkaline earth salts required higher temperatures to produce emission.

Analysis of rain water in Nagoya and Kiryu Cities has been carried out by K. Sugahara[5], and S. Muto[6] respectively. The results show that the most important constituents are sodium and chloride ions with minor constituents such as K, Fe, Al, Ca, Mg, SO_4 and SiO_2.

3) H. A. Barton, G. P. Harnwell, and C. H. Kunsman, *Phys. Rev.*, **27**, 739 (1926).
4) B. Toubes and G. K. Rollefson, *J. Chem. Phys.*, **8**, 495 (1940).
5) K. Sugahara, *Kagaku (Science)*, **18**, 485 (1948).
6) S. Muto, *J. Chem. Soc. Japan*, **74**, 429 (1953).

A few rain drops were collected in a quartz vessel in Kyoto City, February 25,1953 and submitted to measurement. The result obtained $N/W = 1.13 \times 10^{14}$ consists of sodium ions with a small portion of potassium ions. If we neglect the effect of the other salts and simply make use of the calibration curve in Fig. 2, N/W may be turned into a more familiar quantity 0.48 millimol./litre.

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Mikroanalyse Mit Hilfe von Ionenaustauschenden Harzen I. Über Den Nachweis Geringer Menge Des Kobalts Mit Ammoniumrhodanid[1]

Von Masatoshi FUJIMOTO

(Eingegangen am 6. Juni, 1953)

Einleitung. Bedeutend charakteristische Färbungen[2] liefern oft die farblosen oder hellgelben ionenaustauschenden Harze bei Gegenwart von der wässerigen Lösung verschiedenartiger Komplexsalzen. Diese Färbungen, die vielleicht von austauschender Adsorption der Komplexionen auf das Harz herrühren, sind manchmal ganz verschieden von den der wässerigen Lösungen der entsprechenden Komplexsalzen und häufig sehr deutlich. Der Verfasser, während seiner Untersuchung über die Rhodanidkomplexsalzen mit den ionenaustauschenden Harzen, hat gefunden, dass bei Gegenwart des überschüssigen Ammoniumrhodanids selbst kleinste Menge von Kobalt in der Lösung dem anionenaustauschenden Harze eine klare himmelblaue Färbung gab, die man für vorzüglichen Nachweis des Kobalts verwenden konnte.

Das in dieser Untersuchung benutzte anionenaustauschende Harz. Amberlite IRA-400[3]: Das Harz wurde durch zweimaliges Durchlaufen der 2N Salzsäure und destilliertes Wassers in die RCl-Form übergeführt. Die Korngrösse ist ungefähr 30 Maschen von Tyrerschem Normalsieb.

Versuchsanordnung. Man bringt einen Tropfen (0.02 ccm. mit Kapillarpipette) der neutralen oder sauren Versuchslösung auf eine weisse Tüpfelplatte[4], dazu fügt man einige Körnchen von anionenaustauschenden Harze mit einer kleinen Platindrahtöse, danach schüttelt um, und versetzt man mit einem Tropfen der 1M Ammoniumrhodanidlösung[5]. Nach einigen Minuten bis einem Tage, je nach der Kobaltmenge der Probelösung, entsteht am Rande oder über das Ganze der Harzkörnchen eine klare himmelblaue Farbe, welche unter Beleuchtung mit einer elektrischen Lampe von 60 Watt und durch etwa zwanzigfache Vergrösserung mit einer Lupe wohl nachweisbar ist.

Bestimmung der Erfassungsgrenze.

(1) Unter Erfassungsgrenze versteht man bei diesem Versuche solche Kobaltmenge in Gamma ($\gamma = 10^{-6}$ g) in jeder Probelösung, die sich in den zwölf Vertiefungen der Tüpfelplatte findet, wenn unter gleichen Bedingungen alle diese positive Reaktion zeigen, d, h., wenn sie nach einer Stunde klar erkennbare, hell himmelbiaue Färbung am Rande der allen Harzkörnchen geben.

(2) Massflüssigkeit wurde aus der Lösung des extrareinen Kobalt (II)chlorids dargestellt, deren 1 ccm. von der Lösung 78.1 mg. von Kobalt enthielt[6].

(3) Die Resultate der Experimente stehen in Tabelle I.

Daher wurde die Erfassungsgrenze 0.16 γ und die Grenzkonzentration $1 : 1.3 \times 10^5$ für Kobalt an dieser Reaktion festgestellt.

Einflusse der Begleitionen. (1) Eisen (III): Die intensiv blutrote Färbung, die bei Anwesenheit der Eisen (III) salze mit Ammoniumrhodanid auf die Harzkörnchen entsteht, stört stark den Nachweis. Durch Zusatz von überschüssigem Kaliumfluoride entfärben sich die Harzkörnchen sehr leicht unter Bild-

1) Eingebracht in der sechsten Jahrsversammlung der Japanischen Chemischen Gesellschaft, Kyoto, April, 1953.

2) Z. B., vgl. K. Kimura und T. Asano, ***Chemistry and Chemical Industry*** (Kagaku to Kogyo), **2**, 258 (1949).

3) Amberlite XE-98 sowie Dowex 2 wurden gleichfalls benutzt, wobei befriedigende Ergebnisse erhalten wurden.

4) Eine Tüpfelplatte mit zwölf Vertiefungen: Vor dem Gebrauch wurde sie in warmer 1N Salzsäure etwa 10 Min. lange eingetaucht, mit Wasser gewaschen, in einem Luftbad bei 50°C getrocknet, und einige Zeit stehen gelassen.

5) Der Verfasser hat geringe Menge des Eisens mit einer Säule des anionenaustauschenden Harzes (RSCN-Form) von dem Ammoniumrhodanid erfolgreich beseitigt: ***Japan Analyst***, **2**, 360 (1953).

6) Die Menge von Kobalt wurde folgenderweise bestimmt: 1) Wägung als $CoSO_4$: 2) Titration von H^+, die durch eine Säule des kationenaustauschenden Harzes, HR, ausgetauscht wurde.

TABELLE I. DIE RESULTATE DER EXPERIMENTE FÜR ERFASSUNGSGRENZE

Nr.	Menge von Co^{2+} (γ in 0.02 ccm.)	Zeit nach der Mischung (Min.)	Reaktionsresultate 1	2	3	4	5	6	7	8	9	10	11	12
1.	0.016	60	−	−	−	−	−	−	−	−	−	±	−	−
	„	1*	±	±	−	±	+	+	−	+	±	+	±	+
2.	0.16	2	±	±	±	−	±	−	±	±	±	±	−	−
	„	10	+	±	+	±	+	+	±	+	±	+	±	−
	„	60	+	+	+	±	+	+	±	+	+	+	+	+
3.	1.6	0.5–1	+	+	+	+	+	+	+	+	+	+	+	+
	„	10	†††	†††	†††	†††	†††	†††	†††	†††	†††	†††	†††	†††

−: nicht erkennbar, ±: unsicher, +: sicher, †††: intensiv gefärbt.

* 1 Tag nach der Mischung.

ung vom farblosen Komplexfluoride[7].

(2) Nickel (II): Die grössere Menge von Nickel(II)salze färbt die Harzkörnchen gelbgrün und hindert ziemlich den Nachweis. Jedoch, a) durch Verdünnung der Lösung bis zum ungefähr 0.5 prozentigen oder noch kleineren Nickelgehalt[8], und danach b) durch einen Blindversuch, der mit der kobaltfreien Nickelsalze ausgeführt wurde, konnte man die obengenannte Störung fast beseitigen.

(3) Kupfer (II): Eine dunkelbraune Färbung, die auf die Harzkörnchen durch Reaktion von Kupfersalze mit Ammoniumrhodanid entsteht, wurde durch Zusatz der Kristallchen des Kaliumjodids und des Natriumthiosulfats leicht entfärbt.[9]

(4) Mangan (II): Grosser Überschuss der Mangan(II)salze stört nicht den Nachweis.

(5) Chrom (III): Weil Chrom(III)salze bei Anwesenheit des Ammoniumrhodanids das Harzkörnchen nicht färben, stört die intensiv dunkelgrüne bzw. blaue Farbe der Lösung von Chrom(III)salze den Nachweis gar nicht.

(6) Uran (VI) als Uranylacetat: Uranylsalze färben die Harzkörnchen lebhaft gelb, und verhindern die Reaktionsempfindlichkeit. Neben einem Blindversuche miteinandergestellt wurde dieser Nachweis mit genügender Empfindlichkeit ausgeführt.

(7) Anionen: Bei Gegenwart von OH^- oder CN^- findet die Färbung von Harze nicht statt, aber durch Zusatz von 1N Salzsäure konnte man diese Störung leicht beseitigen. Entschieden grosser Überschuss von F^-, I^-, und $S_2O_3^{2-}$ stört nicht den Nachweis. (Vgl. (1) und (3)).

(8) Mineralsäuren: 0.7 mg. Salz-, 1.0 mg. Schwefel-, 1.5 mg. Salpeter-, 7.2 mg. Phosphor-, und 1.2 mg. Perchlorsäuren stören nicht den Nachweis von 0.16 γ Kobaltmenge.

(9) Karbonsäuren: Bei Anwesenheit von 1.8 mg. Essig-, 2.0 mg. Oxal-, 2.0 mg. Wein-, und 1.5 mg. Zitronensäuren wurde der Nachweis von 0.16 γ Kobaltmenge nicht gestört.

Die so erhaltenen Resultate werden in Tabelle II. kurz zusammengestellt.

TABELLE II. EINFLUSSE DER BEGLEITSTOFFE

Begleitstoffe	Menge von Begleitstoffen	Nachweisbare Kobaltmenge	Grenzverhältnis	Anmerkungen
Fe^{3+}	700 γ	0.32 γ	$1:2.2\times10^3$	+KF (überschüssig).
Ni^{2+}	320 γ	0.32 „	$1:10^4$	<Ni 0.5 proz. u. Neben Blindversuche.
Cu^{2+}	1 mg	0.5 „	$1:2\times10^3$	+KI (Kristallchen) +$Na_2S_2O_3$ („ „).
Mn^{2+}	1 mg	0.2 „	$1:5\times10^3$	.....
Cr^{3+}	400 γ	0.32 „	$1:1.3\times10^3$	Neben Blindversuche.
UO_2^{2+}	700 γ	1.6 „	$1:4.5\times10^2$	Neben Blindversuche.
OH^-, CN^-	Grosser Überschuss.	0.16 „	.....	+1N·HCl (überschüss.).
F^-, I^- / $S_2O_3^{2-}$	Grosser Überschuss.	0.16 „	.....	.....
A:	Grosser Überschuss.	0.16 „	.....	.....
B:	Grosser Überschuss.	0.16 „	.....	.....

A: HCl, H_2SO_4, HNO_3, H_3PO_4 und $HClO_4$.
B: Essig-, Oxal-, Wein- und Zitronensäuren.

7) I.M. Kolthoff, *Mikrochemie*, **8**, 176 (1930).
8) F. Feigl, „Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 3. Aufl. 1938, S. 220.
9) M. Ishibashi, „Qualitative chemische Analyse (Teisei Bunseki-Kagaku)," Band 1., 3. Aufl. 1947, (japanisch), S. 237.

Beidem oben ausgeführten Versuche, wurde es auch gefunden, dass in der einigen sogenannten „extrareinen" Probe von Nickel(II)chlorid, Nickel(II)karbonat, und Mangan(II)sulfat eine kleine Menge des Kobalts enthalten war.

Zusammenfassung

1. Der Nachweis von Kobalt mit Ammoniumrhodanid wird verbessert durch die Anwendung von der farblosen oder hellgelben ionenaustauschenden Harzkörnchen, und eine neue Tüpfelmethode wird vorgeschlagen.

2. Nach dieser Methode kann man den Nachweis geringer Menge des Kobalts bei Anwesenheit verschiedenartiger Ionen (Fe^{3+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Cr^{3+}, UO_2^{2+}, OH^-, CN^-, F^-, I^-, und $S_2O_3^{2-}$) sowie der Säuren (HCl, H_2SO_4, HNO_3, H_3PO_4, $HClO_4$, Essig-, Oxal-, Wein-, und Zitronensäuren) ausführen.

3. Wie oben erörtert, hat diese methode die folgenden Vorzüge:

(1) Grössere Empfindlichkeit und leichte Erkennbarkeit,

(2) Mit der Zeit steigende Deutlichkeit der Reaktion (vgl. Tabelle I),

(3) Erhaltbarkeit des Ergebnisses nach dem Trocknen der gefärbten Harzkörnchen,

(4) Ausführbarkeit ohne spezielle Reagenzien und lästige Verfahren,

(5) Ausführbarkeit für saure sowie neutrale Probelösung und seine höhere Spezifität (vgl. Tabelle II), u.s.w..

Zum Schluss möchte der Verfasser Herren Prof. Dr. E. Minami, Dr. M. Honda, und Dr. H. Kakihana für ihre wertvolle Ratschläge bei dieser Untersuchung seinen herzlichen Dank aussprechen.

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Hydrogen Sulfide Cookings of p-Oxybenzyl Alcohols. I.

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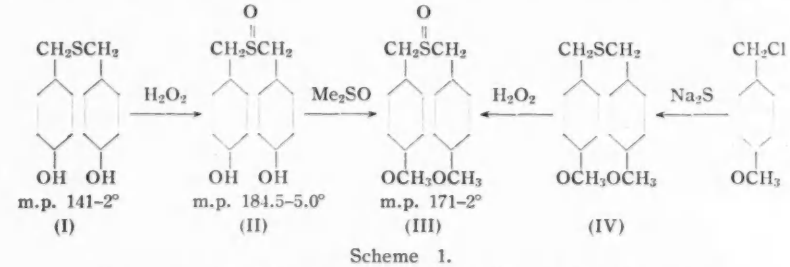
(Received August 3, 1953)

The first experiments on model compounds in connection with the mechanism of kraft cooking processes were made by Enkvist[1]. Among others[2] he obtained a very important result that vanillyl alcohol gives vanillyl disulfide on cooking with an aqueous solution of hydrogen sulfide of *pH* 7 during 72 hours at 100°C. He proposed a theory of mechanism of kraft cooking mainly from the behaviours of vanillyl disulfide against aqueous alkali and his opinion has been generally accepted by the chemists of this field[1)3)].

In connection with the following paper, which deals with the hydrogen sulfide cookings of *p*-oxybenzyl ether, the reactivity of *p*-oxybenzyl alcohol was investigated at first. The expected product 4,4′-dioxydibenzyl disulfide was not obtained but 4,4′-dioxydibenzyl sulfide[1)] was the only product obtainable when *p*-oxybenzyl alcohol was cooked during 6.5 hours or 70 hours. The yields of the monosulfide were 82 and 61% respectively for each cooking hours.

The structure of the monosulfide[1)] was determined by the method shown in the scheme 1. As on methylation of the mono-



Scheme 1.
Determination of the constitution of 4, 4′-dioxydibenzyl sulfide

1) Enkvist and Moilanen, *Svensk Papperstidn.*, **52**, 183 (1949).

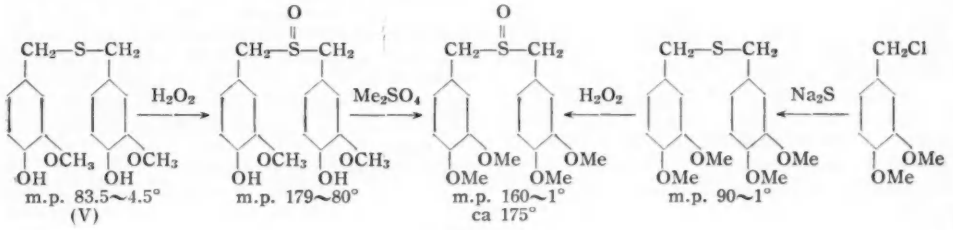
2) Enkvist and Högglund, *festskrift tillägnad* J. Arvid Hedvall, **1948**, 149.

Enkvist, *Svensk Papperstion.*, **51**, 225 (1948).

3) Cf. Higglund, " Chemistry of Wood ", Academic Press Publishers, Inc., New York, N.Y. 1951, p. 484.

sulfide (I) sulfur was split off (probably as dimethyl sulfide) and dianisyl sulfide (IV) was not obtained by this process, that was oxidized at first to sulfoxide (II) and then methylated to dianisyl sulfoxide (III). According to our experience, on methylation of thiolignin with dimethyl sulfate and alkali similar splitting off of sulfur occurs probably as dimethyl sulfide.

As *p*-oxybenzyl alcohol did not give the expected disulfide, vanillyl alcohol was also examined in the similar way. It gave again monosulfide (72%) (V) and a very small amount of divanillyl disulfide as the result of 8 hours cooking. The constitution of divanillyl sulfide was determined in the same way as in 4, 4′-dioxydibenzyl sulfide according to the scheme 2. Diveratryl sulfoxide has two melting points.



Scheme 2.
Determination of the constitution of divanillyl sulfide

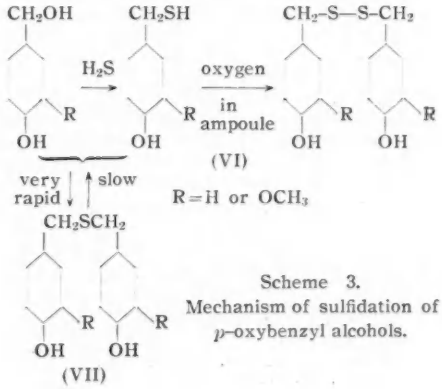
The reactivities of 4, 4′-dioxydibenzyl sulfide (I) and divanillyl sulfide (V) with aqueous alkali were also tested in the same manner as the procedure used by Enkvist in the case of divanillyl disulfide[4]. Monosulfides also split off sulfur as hydrogen sulfide, as is shown in the following table.

Table I. Desulfidation of Monosulfide (I) and (V) with Aqueous Alkali. (5% NaOH, 100°)

	hrs.	splitted.
4, 4′-dioxydibenzyl	3	10.8%
Sulfide (I)	5	88.0%
Divanillyl sulfide (V)	3	19.7%

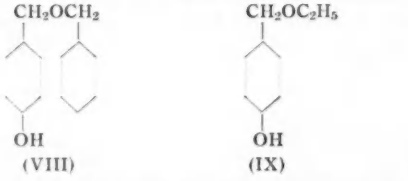
1) On the Mechanism of Sulfidation of *p*-Oxybenzyl Alcohols.

The following mechanism (scheme 3) is assumed to be most probable. At the beginning, hydrogen sulfide reacts with *p*-oxybenzyl alcohol so as to give *p*-oxybenzyl mercaptan (VI), which condenses rather rapidly with the remaining alcohol. The primary reaction product is thus monosulfide (VII). Monosulfide is, however, not completely stable; there it is in equilibrium with the alcohol and mercaptan.



Scheme 3.
Mechanism of sulfidation of *p*-oxybenzyl alcohols.

This assumption is not unreasonable, because, as will be shown in the next paper, benzyl ether linkage is very susceptible of being hydrolysed when it is activated by the phenolic hydroxyl group in its paraposition



(e.g. VIII and IX) and, therefore, the benzyl thioether linkage activated by both hydroxyl groups in 4 and 4′ positions may be surely

4) Enkvist communicated privately a preliminory opinion as follows: The first product in each case will be vanillyl mercaptan. If the solution has a high concentration of hydrosulfide ion and if its *p*H is slightly lower than 7—in his case it was about 5 after the digestions, as he reported previously (cf. (1))—the substance will remain as vanillyl mercaptan until the opening of the tube. Then, the outer air will oxidize it during crystallization to vanillyl disulfide. If the concentration of hydrogen sulfide is slightly less and the *p*H is 7 or slightly higher as in our case, the vanillyl mercaptane will find occasion to react with vanillyl alcohol or sodium vanillyl mercaptide under the formation of vanillyl monosulfide.

hydrolyzable. Molecular oxygen in the air space of glass ampoule will oxidize the mercaptan, which exists in equilibrium with the monosulfide although its concentration is very low. Thus, monosulfide and disulfide are expected in our experiment, as the oxygen in the ampoule is rather limited. The reaction product obtained by Enkvist consisted mainly of disulfide, but this is not explainable by the above mechanism, as according to his private communication the ampoule used by him was not large enougn to supply the necessary amount of oxygen. It is therefore possible that some other unknown factors are determining the course of the reaction; in one case mainly monosulfide and in the other mainly disulfide is obtained as reaction product[4].

2) On the Mechanism of the Kraft Cooking Process.

The monosulfide group of thiolignin had been assumed to be stable to aqueous alkali, but the present results indicate that this group is not stable just as disulfide group, at least when this is activated by both phenolic hydroxyl groups in 4 and 4′ positions. It seems, therefore, to be possible to explain the mechanism of sulfidation of lignin and desulfidation of thiolignin without considering the formation of the disulfide group. The mechanism may be explained more reasonably if the formation of both mono- and di-sulfide groups are taken in consideration. Because the side chain of lignin contains oxygen atoms of various oxidation stages, the formation of the disulfide group by self-oxidation will be easier in the case of lignin than in the model compounds. However, quantitatively speaking, the main part of the sulfur atoms, split off by alkali in the kraft cooking process may exist as a form of monosulfide.

As Mikawa et al. observed[5], X group of lignin was sulfidated with hydrogen sulfide quite rapidly and this reaction was completed after about 5 hours. The velocities of sulfidation of *p*-oxybenzyl alcohol and vanillyl alcohol are not yet clear. But the fact that they are sulfidated to a considerable extent during less than 10 hours cooking will support the opinion that X group of lignin is a benzyl alcoholic hydroxyl group with a phenolic hydroxyl in its para-position.

Experimental Part

1. Hydrogen Sulfide Cooking of *p*-Oxybenzyl Alcohol.

3.7 g. of *p*-oxybenzyl alcohol was added to a solution (final *p*H was adjusted to just 7) of $Na_2S \cdot 9H_2O$ (7.2 g.) in 300 cc. of Clark-Lubs buffer solution (108 g. of KH_2PO_4 and 15 g. of NaOH in 1000 cc. of water). The mixture was heated at 100° for 6.5 hours in a stainless autoclave of just 550 cc. capacity. On cooling, crystals of almost pure 4, 4′-dioxydibenzyl sulfide separated (3.29 g., 82%), which were recrystallized from toluens containing a little dioxane, m.p. 141–2°. Found: S, 12.9%, Calculated for $C_{14}H_{14}O_2S$: S, 13.0%.

The same reaction was performed during 70 hours in a rotating glass ampoule of 150 cc. capacity (*p*-oxybenzyl alcohol 2.0 g., $Na_2S \cdot 9H_2O$ 3 g., buffered hydrogen sulfide water of *p*H 7, 100 cc.). The yield of melting point pure 4, 4′-dioxydibenzyl sulfide was 1.2 g. (61%). 4, 4′-dioxydibenzyl disulfide was not obtained from the reaction mixture.

2. Hydrogen Sulfide Cooking of Vanillyl Alcohol.

The reaction was performed mainly as in the experiment 1 (vanillyl alcohol 2.5 g., $Na_2S \cdot 9H_2O$ 3 g., hydrogen sulfide water 100 cc., 8 hours at 100°, capacity of autoclave just 150 cc.). The separated crystals were filtered off, dissolved in alcohol, passed through a layer of active Al_2O_3, the alcohol was evaporated and the residue was recrystallized from toluene. Yield 1.8 g. (72%), m.p. 83.5–4.5°. This is divanillyl sulfide. Found: S, 10.5; MeO, 19.8, Calculated for $C_{16}H_{18}O_4S$: S, 10.4 MeO, 20.3%.

The mother liquor of this crystal separates after about a week, forming a mixture of large crystals of monosulfide and fine crystals of disulfide, from which the former were separated with a pincette and the latter were dissolved in acetone and purified by reprecipitation by water (50 mg.). It melted at 128–9° and does not show any m.p. depression in admixture with the authentic sample of divanillyl disulfide, which was synthesized according to the method of Manchot and Zahn[6].

3. Syntheses of 4, 4′-Dioxydibenzyl Sulfoxide and Divanillyl Sulfoxide.

4, 4′-Dioxydibenzyl sulfide (100 mg.) was dissolved in 4 cc. of glacial acetic acid, 0.3 cc. of 30% H_2O_2 was added and the solution was set aside over night at the ordinary temperature[7]. The reaction mixture was diluted with water and neutralized with $NaHCO_3$. The separated crystals were filtered, washed with water, dissolved in alcohol and reprecipitated with water, yield 70 mg., m.p. 184.5–5.0°. The analysis agrees with the compound, 4, 4′-dioxydibenzyl sulfoxide. Found: S, 11.8, Calculated for $C_{14}H_{14}O_3S$: S, 12.2%.

Divanillyl sulfoxide was also synthesized similarly from divanillyl sulfide (100 mg.). Yield 50 mg. Found: S, 9.7, Calculated for $C_{16}H_{18}O_5S$: S, 9,95%.

4. Methylation of Sulfoxides.

4, 4′-Dioxydibenzyl sulfoxide or divanillyl sulfoxide (80 mg.) was dissolved in 10 cc. of sodium hydroxide solution (NaOH 0.8 g.). 0.8 cc. of dimethyl sulfate was added and the whole shaken until it disappeared. The separated dianisyl or

5) Mikawa, Sato, Takasaki and Okada, *J. Soc. Chem. Ind. Japan*, **54**, 299 (1951); TAPPI in the press.
Mikawa, *J. Soc. Chem. Ind. Japan*, **54**, 651, 762 (1951).

6) Manchot and Zahn, *Ann.*, **345**, 320 (1906).

7) Hinsberg, *Ber.*, **41**, 2338 (1908).

diveratryl sulfoxide (yields were very good) was filtered, washed and purified by reprecipitation from its acetone solution with water. Their melting points were not depressed in admixture with the authentic samples synthesized according to the experiments 5 and 6.

5. Syntheses of 4, 4′-Dimethoxydibenzyl Sulfide and Sulfoxide.

$Na_2S \cdot 9H_2O$ (2.40 g.) was dissolved as far as possible in alcohol (40 cc.), anisyl chloride (1.56 g.) was added and the whole refluxed for about 30 min.[8]. Water was added to the mixture, extracted with ether, washed with water, the ether was evaporated and the residue (1.5 g.) was distilled at 0.005 mmHg (bath temp. 150°). The residue (0.7 g.) was dissolved in several grams of glacials acetic acid. 0.8 cc. of 30% H_2O_2 was added (during which some heat was evolved), and after about 4 hours poured into water. The precipitated crystals were filtered, washed with water, dried and recrystallized twice from ethyl alcohol containing a little water, m.p. 172–3°. Found: MeO, 20.4; S, 11.3, Calculated for $C_{16}H_{18}O_3S$: MeO, 21.4; S, 11.0%.

6. Syntheses of Diveratryl Sulfide and Sulfoxide.

Veratryl alcohol (3 g.) was converted to chloride according to the method of Freudenberg[9]. The somewhat crude veratryl chloride obtained was subjected to reaction with 2.5 g. of $Na_2S \cdot 9H_2O$ in 80 cc. of alcohol. NaCl was filtered and the filtrate was concentrated in vacuo, water was added and the neutral reaction product extracted with benzene, the benzene extract was dried with Na_2SO_4, the solvent was evaporated and the residue was crystallized from its ether solution by petroleum ether. Recrystallisation from the mixture of benzene and petroleum ether yielded a product (1.0 g.), which melted at 90–1°. The analysis agrees with the theory that the compound is diveratryl sulfide. Found: S, 10.8, Calculated for $C_{18}H_{22}O_4S$: S, 9.6%.

Diveratryl sulfide (100 mg.) and H_2O_2 (30%, 0.4 cc.) was dissolved in 4 c.c. of glacial acetic acid and set aside overnight at the room temperature. Water was added to the solution, neutralized with $NaHCO_3$ and the separated crystals were filtered, dissolved in acetone and reprecipitated with water (70 mg.), which melted at 169.5–70.5° when heated rapidly and at ca. 175° when heated slowly. The analysis agrees with the theory that the compound is diveratryl sulphoxide. Found: S, 9.0, Calculated for $C_{18}H_{22}O_5S$: S, 9.14%.

7. Reactions of 4, 4′-Dioxydibenzyl Sulfide (1) and Divanillyl Sulfide (2) with Aqueous Solution of Alkali.

100 mg. of (1) or (2) was heated at 100° with 5% (cf. reference (1)) aqueous solution of NaOH in a micro-methoxyl apparatus due to Zeisel in the atmosphere of hydrogen. The solution was cooled and acidified with glacial acetic acid and the liberated hydrogen sulfide was swept with hydrogen into dilute NaOH in wash trap and receiver. The combined sodium hydroxidesolution was oxidized with bromine water and SO_4'' was determined as usual. Results obtained are shown in the table.

The author wishes to express his gratitude to the following members of the laboratory, Dr. H. Okada, the head, Miss. S. Suehiro and Mr. K. Sato for their encouragement and help.

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8) Märker, *Ann.*, **136**, 88 (1965).
9) Freudenberg, Carrara and Cohn, *Ann.*, **446**, 87 (1925).

p-Hydroxy-Benzyl Ethers As Lignin Models. II.

Hiroshi MIKAWA

(Received August 3, 1953)

It is now generally accepted that the sulfonatable groups of lignin are not unique and consist of three different types of groups, namely X, Z, and B[1]. The constitutions of these groups are concluded mainly from the experiments on model compounds and the analyses of lignosulfonic acids. Recently Lindgren and Adler gave very useful reviews concerning the sulfonatable groups of lignin[2].

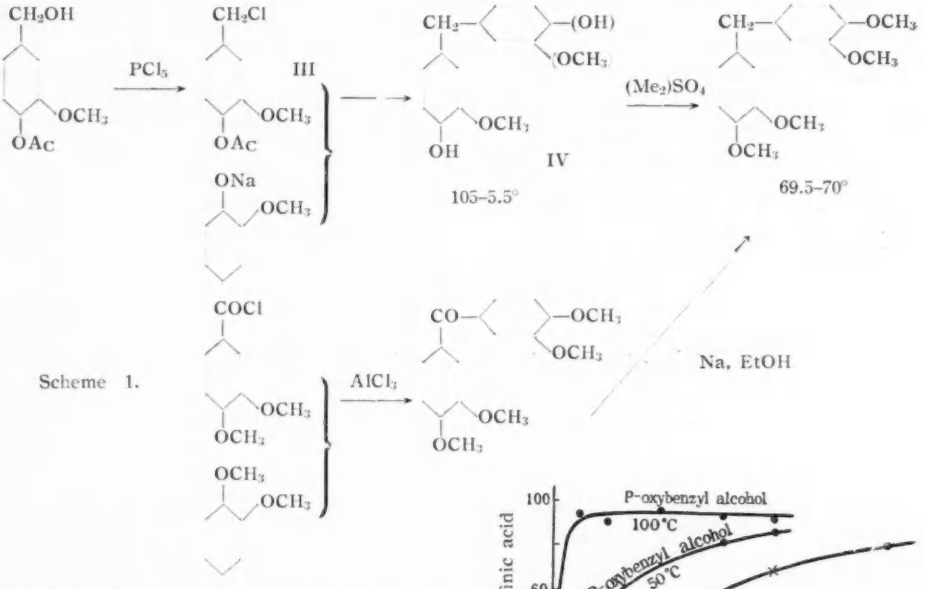
In the present paper the constitution of X group is discussed from the results of the hydrogen sulfide cookings of *p*-hydroxybenzyl ethers as lignin models. A series of experiments of Lindgren, Enkvist, Erdtman, Adler, Leopold and Migita et al. On the sulfonation (rapid sulfonation of *p*-hydroxybenzyl alcohols and slow sulfonation of *p*-methoxybenzyl alcohols[3]) and sulfidation (former compounds

1) Lindgren, *Acta Chem, Scand.* **5**, 603 (1951). Mikawa, Sato, Takasaki and Okuda, *J. Soc. Chem. Ind. Japan*, **54**, 299 (1951); TAPPI in the press. Mikawa, *ibid*, **54**, 651, 741, 762 (1951). **55**, 294, 342 (1952).
2) Lindgren, *Svensk Papperstidn.* **55**, 78 (1952). Adler and Lindgren, *ibid.* 565.
3) Lindgren, *Acta. Chem. Scand.* **1**, 779 (1947); **3**, 1011 (1949). Erdtman and Leopold, *ibid*, **3**, 1358 (1949). Adler and Yllner, *Svensk Papperstidn.* **55**, 238 (1952). Adler, Lindgren and Saeden, *ibid.* **55**, 245 (1952). Migita, Nakano, Ichino and Mikawa, *Tech. Assoc. Pulp and Paper Ind. Japan*, in the press.

react with H_2S[4] but the latter compounds do not[5]) of model compounds have definitely established that X group of lignin must have phenolic OH group in its para position. Though the results of experiments on vanillyl alcohol and *p*-oxybenzyl alcohol suggest that X group is a free benzyl alcoholic group, Lindgren found that pinoresinol is sulfonated comparatively rapidly at higher *p*H[6]) and he pointed out the possibility that X group is the benzyl alkyl ether grouping.

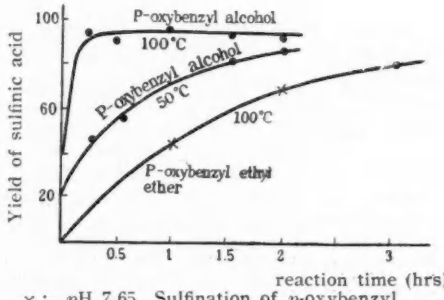
As we have demonstrated, one of the most striking characteristics of X group is its reactivity with H_2S at *p*H 7[1]). It will be, therefore, most desirable to test at the same *p*H the reactivity of H_2S with benzyl ethers which have a phenolic OH group in its para position[7]).

The syntheses of compounds of the type, for example, I is highly desirable for our purposes. Synthesis of II was attempted at first according to scheme 1, but the condensation of sodium guaiacolate and III in toluene (which contains a little alcohol) gave diphenylmethane derivative IV, m.p. 105–5.5°, which on methylation gave 3, 4, 3′, 4′-tetramethoxydiphenylmethane. The melting point, 69.5–70°, of the methylated product of IV was not depressed in admixture with the authentic sample of 3, 4, 3′, 4′-tetramethoxydiphenylmethane (which was synthesized from 3,4,3′,4′-tetramethoxybenzophenone according to the method of Robinson[8]) but showed marked depression with the authentic sample of veratryl guaiacyl ether, m.p. 78–9°. The structure of IV is therefore either 4, 4′-dioxy-3, 3′-dimethoxy- or 4, 3′-dioxy-3, 4′-dimethoxydiphenyl-methane, although, of course, the former structure is by far the more probable.



Scheme 1.

As, therefore, the syntheses of the compounds of type I seemed to be comparatively



×: *p*H 7.65 Sulfination of *p*-oxybenzyl
●: *p*H 6.22 alcohol (5% SO_2, 1% NaOH)
and
p-oxybenzyl ethyl ether (*p*H 6.22 & 7.65)

4) Enkvist and Mollanen, *Svensk Papperstidn.* **52**, 183 (1949). Mikawa, cf. previous paper.
5) Enkvist, unpublished (cf. (2)).
6) Lindgren, *Acta Chem. Scand.* 6, 91 (1952).
7) T. Enkvist made recently profound investigations on the sulphidation of model compounds. cf. *Svensk Papperstidn.* **55**, (1952). In this paper he reaches already the conclusion that the compounds with benzyl ether linkage activated by phenolic OH group in its orth and para position combine with sulfur by hydrosulfide cooking at *p*H 7.
8) Robinson, *J. Chem. Soc.*, **107**, 273 (1915).

TABLE 1. SULFONATIIN OF *p*-OXYBENZYL ETHYL ETHER 100°C

pH	hr 1	2	3
6.22	45.8	—	86.3
7.65	46.4	73.2	—

difficult[9], it was aimed at reaching the compounds of the type V, as it was made clear from the following results (a) and (b) that the methoxyl group in the meta position does not seem to exert any significant effect on the reactivity of the groups in the side chain, which fact Lindgren has already suggested in his review[2].

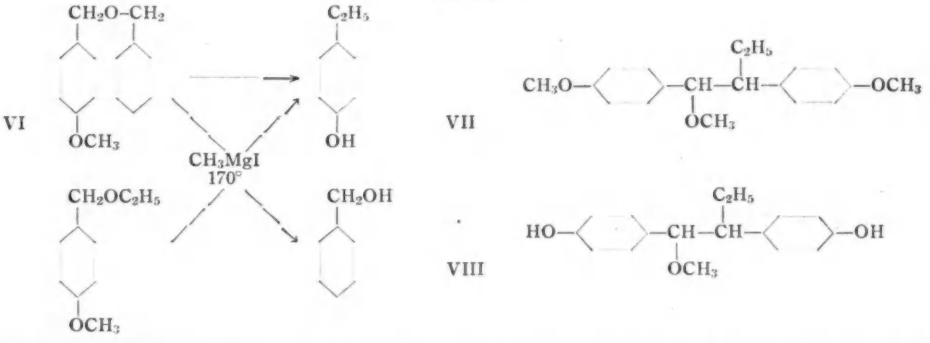
V

(a) *p*-Oxybenzyl alcohol is sulfonated as vanillyl alcohol quite rapidly and almost quantitatively with sulfite solution to give *p*-oxybenzyl sulfonic acid, as is evident from the figure[3].

(b) As was shown in the previous paper, *p*-oxybenzyl alcohol reacts with H_2S at *p*H 7 very easily and 4, 4′-dioxydibenzyl sulfide was obtained, just as vanillyl alcohol is.

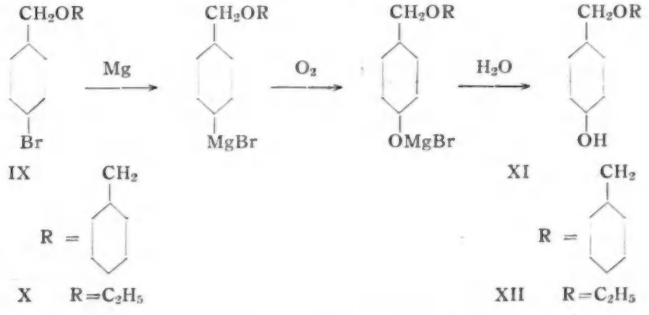
Demethylations of *p*-methoxybenzyl ethers with methyl magnesium iodide were attempted at first[10]. *p*-Methoxydibenzyl ether VI gave a considerable amount of benzyl alcohol and *p*-ethylphenol, when treated with methyl magnesium iodide at 170°. *p*-Methoxybenzyl ethyl ether gave similarly *p*-ethylphenol under the same conditions (see scheme 2). It was therefore made clear that the selective cleavage of arylether linkage of these compounds with the reservation of benzyl ether linkage is fairly difficult under these conditions. T. Takahashi was able, however, recently to demethylate VII to VIII with methyl magnesium iodide[11].

Scheme 2.



At last, *p*-oxybenzyl ethers (XI and XII) were synthesized from the corresponding *p*-bromobenzyl ethers (IX and X) via their Grignard compounds as shown in the scheme 3[12]. The actual Yeilds of XI and XII were 20 and 23% of the theoretical respectively.

Scheme 3.



9) However, B. Leopold synthesized recently vanillyl methyl ether in a very simple way. cf. *Svensk Papperstidn.*, **55**, 816 (1952).

10) Späth, *Monatsh.* **35**, 319 (1914); **36**, 6 (1915). Luttinghaus and Saar; *Angew. Chem.*, **51**, 915 (1938). Kharasch and Huang, *J. Org. Chem.*, **17**, 669 (1952).

11) Takahashi: *J. Chem. Soc. Japan*, in the press.

12) Porter and Steel, *J. Am. Chem. Soc.*, **42**, 2650 (1920). Ivanoff, *Bull. Soc. Chim.*, **1**, 47 (1925). Bert and Dorier, **182**, 63 (1926). Smith, Hoehn and Ungnade, *J. Org. Chem.*, **4**, 351 (1939).

The boiling and melting points of these compounds and the melting points of some of their derivatives were shown in Table II.

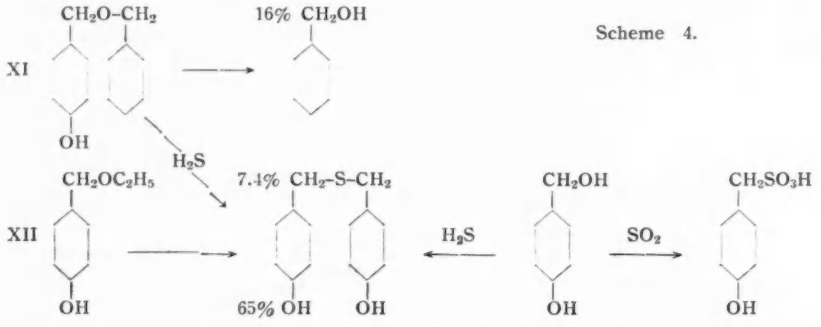
TABLE II.

	b.P., m.p.		*p*-nitrobenzoate	3, 5-dinitrobenzoate	acetate
HO—⟨⟩—CH_2OCH_2—⟨⟩	XI b.p. 0.005	130–5°	m.p. 74–5°	—	m.p. 45.5–6°
HO—⟨⟩—$CH_2OC_2H_5$	X b.p. 0.8	105°	m.p. 74–5°	m.p. 107–8°	—
	m.p.	50–1°			

p-Oxydibenzyl ether XI was sealed in an ampoule with H_2S water of *p*H 7, shaken well and heated for 15 hours at 100°C. Because of the low solubility of this compound the reaction was heterogeneous. 4,4'-dioxydibenzyl sulfide and benzyl alcohol were obtained in the yields of 7.4 and 16% (of the theory) respectively. The former was separated as such and the latter as its 3,5-dinitrobenzoate. The yields were calculated from those of the products of correct melting points.

p-Oxybenzyl ethyl ether XII was treated similarly for 18 hours. Pure 4,4'-dioxydibenzyl sulfide was obtained in the yield of 65% (of the theory). In this case the reaction was homogeneous. These results were shown in scheme 4.

Scheme 4.

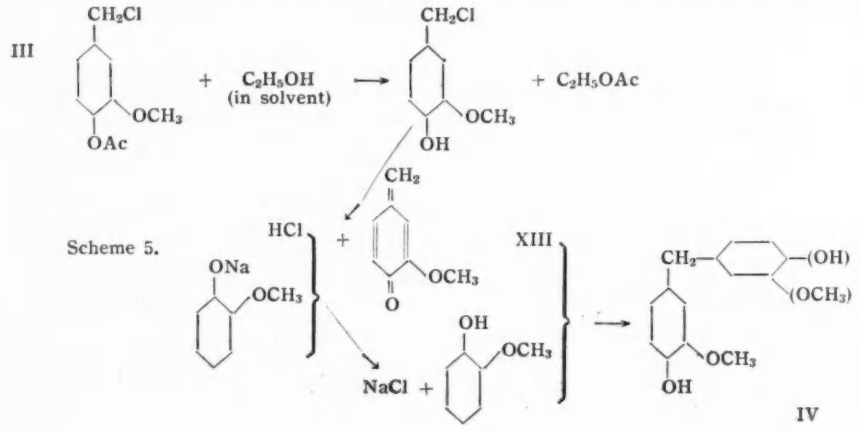


p-Oxybenzyl ethyl ether XII was sulphonated at pH 6.22 and 7.65. As is shown in the figure and Table 1, the sulfonation was very rapid.

Discussion

i) The Condensation of sodium guaiacolate and III in toluene containing a small amount of alcohol to give diphenylmethane derivative IV at comparatively low temperature suggests to us that the reaction has proceeded via the methylene quinone structure XIII as is shown in scheme 5. It is a well known fact,

Scheme 5.



that pseudophenol alcohol halides condense with phenols or dimethylanilines to give diphenylmethane derivatives[13].

ii) No attempt have been made to cleave lignin molecule with grignard reagent of its building stones[14]. As at least about 50% of the building stones of native lignin are thought to be linked through aryl ether linkage between the hydroxyl group of the side chain and the phenolic OH group in its para position[2], it will be very interesting to use grignard reagent to cleave these linkages.

iii) The fact that the *p*-oxybenzyl ethers XI and XII are easily hydrolyzed even at pH 7 at 100°C and react with H_2S to give 4,4′-dioxydibenzyl sulfide is completely in line with the properties of X group[1].

The fact suggests to us again a possibility that this group is a benzyl alkyl ether group with phenolic OH group in its para position. As the sulfidation velocity of X group is approximetely known[1], we will be able to compare the velocity with that of the models, if the latter is measured with sufficient accuracy. It is, therefore, very interesting to measure accurately the sulfidation velocity of model compounds with the so-called dilution method[15] using radioactive mono sulfide.

p-Oxybenzyl ethyl ether was sulfonated with neutral sulfite solutions and moreover the velocities of sulfonation do not seem to depend on the pH values. These findings are also completely parallel with the properties of X group.

Added in proof. According to the private communication of Dr. J. de Jonge, Philips Research Laboratories, Holland, our sample of *p*-hydroxybenzyl ethyl ether was hydrolyzed very quickly. i.e., at pH 6.8 after 3 hours and at pH 5.2 after 6 hours it was completely hydrolyzed into *p*-hydroxybenzyl alcohol at 100° and somewhat less completely at pH 8.1 after 6 hours at 100°. It may, therefore, safely be concluded that in the reaction with H_2S hydrolysis of ether to the corresponding alcohol predeeds the formation of the sulfide.

Experimental Part

1. Synthesis of 3-Methoxy-4-acetoxybenzyl Chloride. Acetylvanillin was reduced to acetylvanillyl alcohol according to the method used by Carothers and Adams[16]. 0.2 g. of $PtO_2 \cdot H_2O$ (according to Adams et al.[17]) was added to a solution of acetylvanillin (14 g.) and $FeCl_2$ (0.5 cc. of 0.2 mol. solution) in 200 cc. of absolute ethanol and was shaken with hydrogen (4 atm.) until no more hydrogen was absorbed. Acetylvanillyl alcohol (11.2 g.) was obtained as a very viscous oil.

2 g. of this acetylvanillyl alcohol was dissolved in 20 cc. of dry chloroform and pulverized PCl_5 (2 g.) was added slowly (during which some heat and HCl gas were evolved). The chloroform solution was washed well with water, dried with Na_2SO_4, the solvent removed in vacuo and the residue (1.9 g.) crystallized from petroleum ether (1.0 g.). The product obtained melted at 46–7° and the analyses agree with the compound being 3-methoxy-4-acetoxybenzyl chloride. Found: Cl, 15.9; CH_3O, 14.0, Calculated for $C_{10}H_{11}O_3Cl$: Cl, 16.6; CH_3O, 14.4%.

2. Condensation of 3-Methoxy-4-acetoxybenzyl Chloride with Sodium Guaiacolate. Sodium (1.1 g.) was dissolved in 20 cc. of anhydrous ethanol and guaiacol (7 g.) and toluene (40 cc.) were added. 3-Methoxy-4-acetoxybenzyl chloride (8 g.) was dissolved in toluene (70 cc.). The two solutions were mixed at once and the whole was warmed at 40° for 30 minutes, the rest stood over-night and was poured into a dilute solution of NaOH and well shaken. Neutral fraction (4.22 g.) was extracted with ether. The aqueous layer was acidified, extracted with ether, and the solvent removed. The residue (6.1 g.) solidified on standing, which was rubbed on a clay plate, dissolved in ether, passed through active Al_2O_3, ether removed and recrystallized from benzene to give white needles (4.06 g.), m.p. 105–5.5° (I).

(I) was methylated with dimethyl sulfate and alkali and recrystallized from aqueous ethanol to give white leaflets, melting at 69.5–70° (II), which was not depressed in admixture with the authentic sample of 3, 4, 3′, 4′-tetramethoxydiphenylmethane. (I) was therefore either 4, 4′-dioxy-3, 3′-dimethoxydiphenylmethane or 4, 3′-dioxy-3, 4′-dimethoxydiphenylmethane. The methoxyl values of (I) and (II) and the mixed melting points of them with several compounds are as follows:

(I), m.p. 105–5.5°, mixed melting point with vanillyl alcohol, 90–2°. Found: CH_3O, 23.5, Calculated for $C_{15}H_{16}O_4$: CH_3O, 23.8%.

(II), m.p. 69.5–70°, mixed melting points with diveratryl ether and veratryl guaiacyl ether, 54–7° and 58–61° respectively. Found: CH_3O, 42.5, 42.6, calculated for $C_{17}H_{20}O_4$: CH_3O, 43.0%.

3. Synthesis of Veratryl Guaiacyl Ether. Veratryl chloride was synthesized according to the method of Freudenberg[18]. Metallic sodium (0.31 g.) was dissolved in 100 cc. of absolute ethanol, guaiacol (2 g.) added, a solution of veratryl chloride (2.2 g.) in 10 cc. of benzene added and the whole was refluxed for 1 hour. The neutral fraction of the product was recrystallized from alcohol (1.5 g.), m.p. 78–9°. The analysis shows that the compound is veratryl guaiacyl ether. Found:

13) Richter-Anshütz: "Chemie der Kohlenstoffverbindungen" Leipzig 1935, Bd. II₂ Seite 371.
14) Brauns, "Chemistry of Lignin" New York 1952, page 574.
15) Wahl and Bonner: "Radioactivity Applied to Chemistry" New York 1951, page 94.
16) Carothers and Adams, *J. Am. Chem. Soc.*, **46**, 1680 (1924).
17) Adams, Voorhees and Shriner, *Org. Synth.* **8**, 92 (1928).
18) February, Carrara and Cohn, *Ann.* **446**, 47 (1925).

CH_3O, 33.7; Calculated for $C_9H_{11}O_4$: CH_3O, 33.9%.

4. Synthesis of *p*-Oxybenzyl Sulfonic Acid. *p*-Oxybenzyl alcohol (3.02 g.) was dissolved in a sulfite solution containing 5 and 1% of SO_2 and NaOH respectively and heated in an autoclave at 100° for 1 hour. The solution was boiled in vacuo, filtered, passed through ion exchange resin IR 120, boiled again in a vacum, neutralized with excess $BaCO_3$, filtered and the solution of the barium salt was evaporated to dryness. The residue was leached with a little water, filtered and again evaporated to dryness. The residue was extracted with ethanol, which contains a little water, ether was added and the precipitated barium salt was filtered (4.0 g.). The analysis shows that the compound is a salt of *p*-oxybenzyl sulfonic acid. Found: Ba, 26.8; Calculated for $C_7H_7O_4SBa_{1/2}$: Ba, 26.8%.

1.0 g. of the barium salt was dissolved in water, passed through ion exchange resin IR 120, the same pyridine added and the whole was evaporated to dryness in vacuo. The residue was recrystallized from a mixture of dioxane acetone and alcohol to give pyridinium salt of *p*-Oxybenzyl sulfonic acid (0.8 g.) m.p. 129–30°. Found: S, 13.0, Calculated for $C_{12}H_{13}O_4NS$: S, 12.0%.

5. Synthesis of *p*-Methoxydibenzyl Ether. 4.2 g. of sodium was dissolved in a solution of anis alcohol (50 g.) in toluene (50 cc.) and when almost all of the metal disappeared, 20 g. of anis alcohol was added in order to complete the reaction. A solution of benzyl chloride (22.7 g.) in 30 cc. of toluene was then added and the mixture refluxed for 1 hour. The toluene solution was washed with water, dried with Na_2SO_4, the solvent removed, and the residue was distilled repeatedly in a vacuum in order to remove anis alcohol as far as possible. The yield of *p*-methoxydibenzyl ether of $bp_{0.8}$ 155–60° was 22 g. Found: CH_3O, 13.1, Calculated for $C_{15}H_{15}O_2$: CH_3O, 13.6%.

6. Attempted Demethylation of *p*-Methoxybenzyl Ethyl Ether to *p*-Oxybenzyl Ethyl Ether. *p*-Methoxybenzyl ethyl ether (1.7 g.) was added to a solution of methyl magnesium iodide, which was prepared from 8.5 g. of methyl iodide, 1.45 g. of magnesium and 50 cc. of ether. The ether was distilled off and the residue was heated in an oil bath for 2 hours (the temperature was raised during 1 hour to 170° and kept at that temperature for 1 hour). On cooling, the residue solidified. This was decomposed with a concentrated aqueous solution of NH_4Cl, acidified and extracted with ether. The ether extract was shaken with dilute alkali, acidified, extracted with ether, dried with Na_2SO_4, the solvent removed and the phenolic residue was converted to its *p*-nitrobenzoate. Repeated recrystallizations from ethanol yielded a product of m.p. 80–1°, not depressed in admixture with *p*-nitrobenzoate of *p*-ethylphenol (m.p. 80–1°) obtained from *p*-methoxydibenzyl ether, when it was decomposed with methyl magnesium iodide (see experiment 7).

7. Attempted Demethylation of *p*-Methoxydibenzyl Ether to *p*-Oxydibenzyl Ether. *p*-Methoxydibenzyl ether (2.19 g.) was added to a solution of methyl magnesium iodide, which was prepared from 8.5 g. of methyl iodide, 1.45 g. of magnesium and 50 cc. of ether. The ether was distilled off and the residue was heated as in the experiment 8. The residue was decomposed with a concentrated aqueous solution of NH_4Cl, acidified and extracted with ether, the solvent removed and the residue (2.01 g.) was separated into neutral (I) and phenolic (II) fractions.

(I) was distilled in a vacuum and the distilled oil (0.84 g.) converted to its *p*-nitrobenzoate, which melted after recrystallization from ethanol at 82–3° (1.4 g.), not depressed in admixture with the authentic *p*-nitrobenzoate of benzyl alcohol (82–3°).

(II) was also distilled in a vacuum and the distilled oil (0.65 g.) converted again to its *p*-nitrobenzoate, which melted after recrystallization from ethanol at 80–1° (0.9 g.), not depressed in admixture with the *p*-nitrobenzoate obtained in the experiment 8. A part of this *p*-nitrobenzoate was hydrolysed with ethanolic NaOH and converted as usual to the carboxymethyl ether, which melted after recrystallization from water at 96–6.5°. These melting points agree well with those of *p*-ethylphenol[19].

8. Synthesis of *p*-Bromodibenzyl Ether. 3g. of potassium was dissolved at the boiling point of toluene in 20 g. of benzyl alcohol, which was diluted with 20 g. of toluene. When almost all of the metal disappeared, 2 g. of K, 5 g. of benzyl alcohol and 5 g. of toluene were added and the reaction was completed. 27 g. of *p*-bromobenzyl bromide in 40 cc. of toluene, which was boiled in a vacuum in order to expel a trace of HBr, was added at once to the suspension of the alcoholate. During ca. 1/2 hours the mixture was maintained at its boiling temperature. Water was added and the reaction product was taken up in ether. The solvent was driven off and the residue was fractionary distilled in a vacuum. The yield of *p*-bromodibenzyl ether of $bp_{0.8}$ 142–45°C was 28 g. (92.5%). Found: Br, 28.9, Calculated for $C_{14}H_{13}OBr$: Br, 28.9%.

9. Synthesis of *p*-Oxydibenzyl Ether. A solution of *p*-bromodibenzyl ether (27.6 g.) and ethyl bromide (10.9 g.) in 90 cc. of ether was gradually added during 5 hours to magnesium in a three necked flask, which was equipped with a dropping funnel, stirrer and a reflux condenser. After the reaction was completed, dry oxygen was bubbled through the reaction mixture for 2.5 hours (during which process some heat was evolved and the solution was separated gradually into two layers). All of the reaction products were decomposed with concentrated aqueous solution of NH_4Cl and then with dilute HCl. The products were extracted exhaustively with ether and separated into neutral (16.0 g.) and phenolic (5.5 g.) fractions. The latter was distilled in a high vacuum. Almost all of the oil (yield 4.3 g., 20% of the theoretical) was distilled at a very constant tmperature of 130–5° 0.005 mmHg.

p-Nitrobenzoate: This was synthesized as usual with *p*-nitrobenzoyl chloride and pyridine

19) McElvain: "The Characterisation of Organic Compounds" New York 1949, page 251.

and recrystallized from methanol. It melted at 74–5°.

Acetate: This was synthesized as usual with acetic anhydride and pyridine and recrystallized from methanol containing a little water. It melted at 45.5–46°. Found: CH_3CO, 16.9, Calculated for $C_{14}H_{14}O_2$: CH_3CO, 16.8%.

10. Synthesis of *p*-Oxybenzyl Ethyl Ether. A solution of *p*-Bromobenzyl ethyl ether (21.5 g.) and ethyl bromide (10.9 g.) in 85 cc. of ether was added dropwise during 2 hours to magnesium (5 g.) in a three necked flask in an atmosphere of hydrogen (during which the content separated into two layers, but the oily heavier layer did not disturb the reaction, because this was not so viscous). After the reaction was completed, the content was evaporated in order to expel hydrogen. Dry oxygen was then passed through the mixture (during which time a very viscous grayish colored mass was deposited, which was stirred frequently during the oxidation). After about 2 hours, the entire content was decomposed with concentrated aqueous solution of NH_4Cl and then acidified with dilute HCl, and extracted with ether. The ether extract was shaken with dilute NaOH solution, which was acidified and extracted again with ether, the solvent removed, and the residual oil (4.63 g.) distilled in a high vacuum. Almost all the oil distilled at 105°/0.8 mmHg (3.9 g., 23% of the theoretical), which solidified the next day, m.p. 50–1°. The analysis shows that the compound is *p*-oxybenzyl ethyl ether. Found: C_2H_5O, 28.8, calculated for $C_9H_{12}O_2$: C_2H_5O, 28.6%. *p*-Nitrobenzoate: m.p. 74–5°. Found: C_2H_5O, 14.5, Calculated for $C_{16}H_{15}O_5N$: C_2H_5O, 15.0%. 3, 5-Dinitrobenzoate: m.p. 107–8°. Found: C_2H_5O, 13.5, Calculated for $C_{16}H_{14}O_7N$: C_2H_5O, 13.0%.

11. Hydrogen Sulfide Cooking of *p*-Oxydibenzyl Ether. *p*-Oxydibenzyl ether (1.05 g) was added to a solution of $Na_2S{\cdot}9HO$ (1.2 g.) in 100 cc. of Clark-Lubs buffer solution (final pH was adjusted to just 7). The mixture was heated in a glass ampoule at 100° for 15 hours (during which the ampoule was shaken vigorously). Because of the low solubility of the phenol the reaction was heterogeneous. After the reaction the organic materials were extracted with ether. The ether extract was dried, the solvent removed, and the faintly pink coloured residual oil (1.10 g.) was let to stand for crystallization. After several days a small amount of crystals separated. Ca. 1 cc. of petroleum ether was added, which did not mix with the oil, and the mixture was kept in a refrigerator further 2–3 days (during which time the amount of the crystalls increased). They were filtered and weighed (50 mg.) (I). The filtrate was diluted with benzene and kept again in a refrigerator to give further 0.13 g. of crystalline material (II), which was filtered and the mother liquor so obtained was separated into phenolic (III) and neutral fractions (IV) which weighed 0.53 and 0.38 g. respectively.

(I) was recrystallized from aqueous ethanol to give leafy plates (40 mg.), m.p. 170.5–71°, which was soluble in dil. NaOH. This was not investigated further.

(II) was also recrystallized from aqueous ethanol, to give 5 mg. or (I) and 50 mg. of 4, 4′-dioxydibenzyl sulfide, having m.p. and mixed m.p. 139–40°.

(III) was acetylated with pyridine and acetic anhydride. 70 mg. of *p*-acetoxydibenzyl ether of correct m.p. was recovered.

(IV) was converted to its 3, 5-dinitrobenzoate, which was recrystallized from ethanol to give 300 mg. of 3, 5-dinitrobenzoate, of benzyl alcohol, having m.p. and mixed m.p. 113–13.5°.

12. Hydrogen Sulfide Cooking of *p*-Oxybenzyl Ethyl Ether. *p*-Oxybenzyl ethyl ether (0.76 g.) was added to a solution of $Na_2S{\cdot}9H_2O$ (1.2 g.) in 100 cc. of Clark-Lubs buffer solution (pH was adjusted to just 7). The mixture was heated in a glass ampoule at 100° for 18 hours (during which time the phenol went into solution and the reaction proceeded in a homogeneous phase). On cooling, beautiful crystalls of 4, 4′-dioxydibenzyl sulfide separated (final pH of the solution was 7.2), which was filtered (0.61 g.) and recrystallized three times from aqueous ethanol (450 mg.), m.p. and mixed m.p. 139–40°. The yield was 65% of the theory.

13. Sulfonation of *p*-Oxybenzyl Ethyl Ether at Various pH (cf. figure). *p*-Oxybenzyl ethyl ether was dissolved (concentration 0.056 mol/l) in a sulfite solution (total SO_2 5%, pH 6.22 or 7.65, 35 cc.), heated at 100° for 1–3 hours in a glass ampoule. The whole content was passed through ion exchange resin IR 120, to remove cations. 7 cc. of 1N H_2SO_4 was added, boiled in vacuo to expel SO_4, 40 cc. of saturated solution of $Ba(OH)_2$ was added, filtered and passed again through IR 120. The solution so obtained was titrated with 1/10 N NaOH with methyl red as an indicator. Results were shown in the figure and Table 1.

The author wishes to express his gratitude to Messrs. M. Takahashi and T. Takahashi at the Tokyo University for their kind advice and to the follwoing members of the laboratory, Dr. H. Okada, Miss S. Suehiro and Mr. K. Sato for their encouragement and help.

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Terminally Phenylated Conjugated Unsaturated Ketones II.[1] *Silver Acetate on Dibenzylidenecycloalkanone Tetrabromides*

Ping-Yuan YEH

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In the course of a study of the aromatization of 2,6-dibenzylidenecyclohexanone[2] the action of silver acetate on dibenzylidenecycloalkanone tetrabromides was studied.

Diacetoxy-dibromo-2, 5-dibenzylidenecyclopentanone was obtained by the action of silver acetate on 2,5-dibenzylidenecyclopentanone tetrabromide in acetic acid even when 4 mole equivalents of silver acetate were used. The corresponding tetraacetoxy-derivative was obtained, however, when 4 mole equivalents of silver acetate were reacted with 2,6-dibenzylidenecyclohexanone tetrabromide. On using 2 mole equivalents of silver acetate and heating them at 85~90° for an hour, both diacetoxydibromo- and triacetoxymonobromo-derivatives were obtained with a 10% recovery of 2, 6-dibenzylidenecyclohexanone tetrabromide. If the temperature was maintained at 85~90° for more than 2 hours or the reaction mixture was refluxed for half an hour the only crystalline product identified was 2,6-dibenzylidenecyclohexanone. By refluxing half an hour in acetic acid, however, tetraacetoxy- and tetrabromo-2,6-dibenzylidenecyclohexanone did not give 2,6-dibenzylidenecyclohexanone.

Two isomers of diacetoxy-dibromo-2,5-dibenzylidenecyclopentanone, m.p. 213~214° (decomp.), colorless plates, and m.p. 185~186°, colorless prisms, and two isomers of tetraacetoxy-2,6-dibenzylidenecyclohexanone, m.p. 227~228° (decomp.), colorless needles, and m.p. 220~221° (decomp.) colorless polygonal crystals, were obtained in the present work.

Experimental[3]

Materials. 2, 5-Dibenzylidenecyclopentanone tetrabromide and 2, 6-dibenzylidenecyclohexanone tetrabromide were prepared according to the published methods[4][5] and had m.p. 175° (with decomposition) and 193°, respectively.

Action of silver acetate on 2, 5-dibenzylidenecyclopentanone tetrabromide. A mixture of 20 g. (0.034 mole) of 2, 5-dibenzylidenecyclopentanone tetrabromide, 24.2 g. (0.136 mole) of silver acetate, and 180 ml. of glacial acetic acid was refluxed for 3 hours under mechanical stirring. After removing the silver bromide and adding water the crude diacetoxydibromo-derivative separated out as a white precipitate (14.0 g., 76%) which was recrystallized from ethanol; colorless plates, m.p. 213–214° (decomp.). It gave positive Beilstein test. *Anal.* Calcd. for $C_{23}H_{22}O_5Br_2$: C, 51.32; H, 4.12. Found: C, 51.78 and 51.63; H, 4.27 and 3.96.

From the mother liquor of the above recrystallization, a small number of colorless prismatic crystals, m.p. 185–186°, were obtained. These also gave positive Beilstein test. *Anal.* Calcd. for $C_{23}H_{22}O_5Br_2$: C, 51.32; H, 4.12. Found: C, 50.84; H, 3.70.

Action of silver acetate on, 2, 6-dibenzylidenecyclohexanone tetrabromide. a) 2, 6-Dibenzylidenecyclohexanone tetrabromide (15 g., 0.025 mole), silver acetate (8.4 g., 0.05 mole), and 70 cc. of glacial acetic acid were heated at 85–90° for an hour and treated in the same manner as in the above experiment. By extracting the silver bromide precipitate with benzene, 10% (1.5 g.) of the unreacted tetrabromide was recovered. The crude product (12.7 g., 90%) was recrystallized from ethanol. Colorless needles, m.p. 210–211° (decomp.). Yield 5.7 g. (40%). It gave positive Beilstein test. *Anal.* Calcd. for $C_{24}H_{24}O_5Br_2$: C, 52.19; H, 4.38. Found: C, 52.52 and 51.94; H, 4.50 and 4.38.

From the mother liquor of the above recrystallization colorless polygonal crystals melting at 200–201° (0.2 g.) were obtained which gave positive Beilstein test. *Anal.* Calcd. for $C_{23}H_{27}O_7Br$: C, 58.76; H, 5.12. Found: C, 58.28; H, 4.78.

When the reaction mixture was refluxed for half an hour or heated at 85–90° for more than 2 hours, instead of heating for an hour, the crystalline product was 2, 6-dibenzylidenecyclohexanone, (m.p. and mixed m.p. with authentic specimen, 117–118°, no depression) and no diacetoxydibromo-derivative could be obtained. *Anal.* Calcd. for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.23; H, 6.51.

b) A mixture of 15 g. (0.025 mole) of 2, 6-dibenzylidenecyclohexanone tetrabromide, 16.8 g. (0.1 mole) of silver acetate, and 200 ml. of glacial acetic acid was refluxed for an hour under mechanical stirring and treated in the same manner as in the above experiment. The precipitate (3.8 g.) thus obtained was recrystallized from benzene. Colorless needles, m.p. 227–228° (decompn.), yield 3.3 g. (26%). This gave negative Beilstein test. *Anal.* Calcd. for $C_{28}H_{30}O_4$: C, 65.87; H, 5.92. Found: C, 66.32; H, 5.95.

1) Ping-Yuan Yeh, "Isomerization and dimerization of 2,6-dibenzylidenecyclohexanone" J. Taiwan Pharmaceutical Association, **5**, 2 (1953).

2) Ping-Yuan Yeh, "Aromatization of 2,6-dibenzylidenecyclohexanone". In this series of manuscript.

3) All melting points are corrected.

4) D. Vorländer and K. Hobohm, *Ber.*, **29**, 1837 (1896).

5) C. E. Garland and E. E. Reid, *J. Am. Chem. Soc.*, 2336 (1925).

Besides this product, some colorless polygonal crystals (less soluble in benzene than the needles, m.p. 220–221° (decomp.), yield 0.3 g. (2.3%), were obtained. These also gave negative Beilstein test. *Anal.* Calcd. for $C_{28}H_{30}O_4$: C, 65.87; H, 5.92. Found: C, 66.19; H, 5.83.

Summary

The action of silver acetate on 2,6-dibenzylidenecyclohexanone tetrabromide and 2,5-dibenzylidenecyclopentanone tetrabromide was studied.

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Deformation of the Regenerated Cellulose Fibers III. Deformation and Refractive Indices of Air-Dried Filament

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This problem has already been studied by one of these authors and it was found[1] that the refractive indices of the air-dried filament change by stretching according to the first theory of Kratky or sometimes according to the second theory or along some courses between the two limits. Of course it was only in the early stage of deformation (v_d<1.4) that the second theory can be applied with a good conformity. The cause of this variation has not been found and here the study was continued and it was found that the deformation can be rather satisfactorily explained by the first theory of Kratky and the irregularity in the early stage is related to the drying condition of the fresh filament.

Experiment

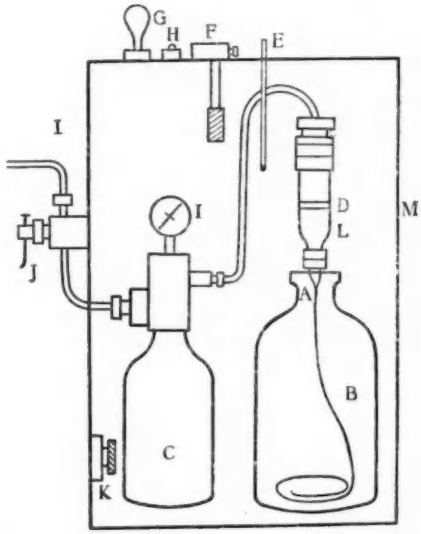
(1) **Model Filament.** A sample of commercial raw ramie was purified by extracting with ether, alcohol and then boiled in 1% NaOH solution repeatedly and bleached. The average degree of polymerization, DP, of it was about 1000.

The purified ramie was then hydrolysed with N-H_2SO_4 at 60°C for some time, followed by boiling with a 1% NaOH solution. Three samples of DP 1000, 540 and 350 were prepared by controlling the duration of hydrolysis.

These samples were dissolved in the cuprammonium solution and spun into isotropic filament of regenerated cellulose. For this purpose the cellulose was placed in a small flask having a thick wall with appropriate amounts of $Cu(OH)_2$ and NH_3-solution and its dissolution was accelerated by kneading in an atmosphere of H_2 which was supplied to the flask through a layer of conc. NH_3-solution. A glass rod (stirrer) was inserted into the flask and was connected to the flask at the mouth elastically and air-tightly by means of a rubber tube.

1) S. Okajima, *J. Soc. Chem. Ind. Japan*, **48**, 86 (1945).

The spinning apparatus was placed in a closed air thermostat as shown in Fig. 1. In the figure,



A: Nozzle
B: Coagulating bath
C: Air tank
D: Oil
E: Thermometer
F: Thermoregulater
G: Signal lamp
H: Switch
I: Manometer
J: Valve
K: Heater
L: Spinning Solution
M: Air thermostat

Fig. 1. Spinning Apparatus

A is a glass nozzle of 0.2~0.3 mm diameter and B, the coagulating bath, is an aq. solution of NaOH (5%). The spinning solution, L, is kept from contact with the atmospheric oxygen by covering with a thin layer of oil D. The pressure added on L was 0.2~0.4 atm. according to the viscosity of the spinning solution. This apparatus was also used in the experiments reported in the preceding

communications on the same problem.[2]

The coagulated filament, which was deposited on the bottom of B, was taken out of B and de-coppered at 25~30°C for 70 min. with a solution containing 200 g. of Na_2SO_4 and 50 g. of CH_3COOH per litre. As the regeneration is followed by a remarkable longitudinal shrinkage of the filament, it was carefully carried out under a condition that allows free shrinkage in order to keep it from the slightest tension at the regeneration.

TABLE 1

Filament No.	Composition of the spinning solution			Temp., °C	DP of the filament
	Cellulose, %	Cu, %	NH_3, %		
S-1	13.6	5.9	18.7	25	270
S-6	11.8	5.5	21.5	30	380
S-10	8.0	3.6	12.0	20	380
S-11	8.0	3.6	12.0	30	370
S-14	12.4	4.9	10.1	30	380
S-15	9.2	3.1	6.1	25	370
S-20	3.0	1.5	8.0	20	580
S-21	8.0	3.0	10.0	25	470

The spinning conditions and some of the properties of the model filaments thus obtained are summarized in Tab. 1.

(2) **Stretching of the Model Filament.** A model filament of about 1 meter length was air-dried under a very slight tension, but being sufficient to prevent the curling up. This is designated as "isotropic filament" in this paper, although it has a small intrinsic double refraction. This slight anisotropy is of course corrected in the calculation of the final stretching degree v_d as is described later.

The air-dried isotropic fiber of known length, l_{0d}, was elongated by hanging overnight a weight W at the lower end and the residual length, l_{2d} was read after removing the weight and waiting until the equilibrium state was obtained (after 1 day). The stretching degree, v_d, was then l_{2d}/l_{0d}. Various amounts of v_d were obtained by changing the value of W. The maximum amount of v_d is a function of the air humidity around the filament as shown in Fig. 2. It was very difficult to carry out the stretching in the relative humidity lower than 60% in our case.

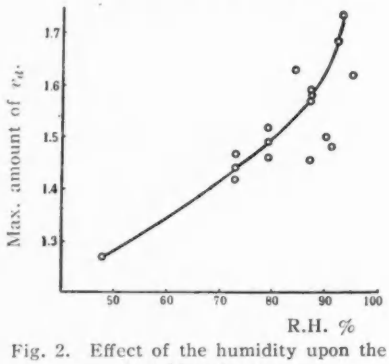


Fig. 2. Effect of the humidity upon the stretching degree.

(3) **Double Refraction.** The stretched filaments were dried in vacuum at 60°C and their refractive indices $n_\parallel$ and $n_\perp$ were measured by Becke's method and corrected as already reported by the authors.[3] The intrinsic double refraction is then given by $n_\parallel - n_\perp$.

Experimental Results

(1) Effect of the Temperature of Spinning.—The samples S-10 and -11 were spun from the same spinning solution under the same conditions except the temperatures only, which were 20 and 30°C respectively. But the effect of this temperature difference can not be observed and the curves follow well the first theory as shown in Fig. 3.

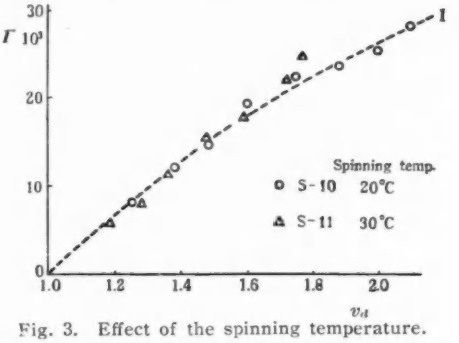


Fig. 3. Effect of the spinning temperature.

In the figure the values of v_d are corrected so as the first point of each curve is placed on the theoretical curve 1 which was calculated on the assumption of the first theory of Kratky.

(2) Effect of the NH_3-concentration in the Spinning Solution.—The spinning solutions of S-6, -14 and -15 are of different

2) S. Okajima, *Bull. Yamagata University*, 1950, No. 1, 21; S. Okajima and Y. Kobayashi, This Bulletin, **24**, 85 (1951); S. Okajima and S. Hayama, ibid, **24**, 90 (1951).

3) S. Okajima and Y. Kobayashi, *J. Soc. Chem. Ind. Japan*, 1943, **46**, 941; S. Okajima, *Bull. Yamagata University*, 1950, No. 1, 21.

NH_3-concentration, while their DP are equal to each other. The solutions of the latter two were evacuated for some time after preparing by the ordinary recipes and the NH_3-concentration was lowered to 10.1 and 6.1% form the original concentrations of 18 and 10% respectively.

The deformations of these filaments are also similar to that of the highest concentration, S-6, and all three coincide with curve 1. (rf. Fig. 4).

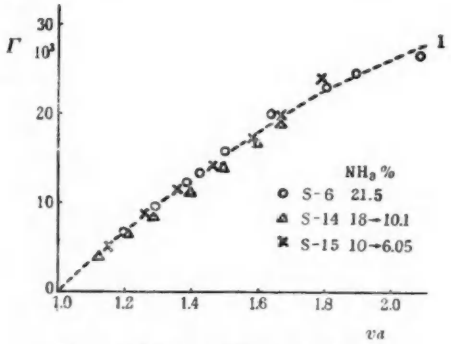


Fig. 4. Effect of NH_3-concentration.

(3) Effect of the Cellulose Concentration of the Spinning Solution.—A series of filaments were prepared from the spinning solution of varying cellulose concentration from 3.0 to 13.6%. Of course DP of the cellulose in the solution was higher in the case of the lower concentration and vice versa for the sake of keeping the viscosity of the solution within comparatively narrow limits, which was necessary for the smooth spinning.

It is seen from Fig. 5 that all the curves are in the vicinity of the theoretical curve

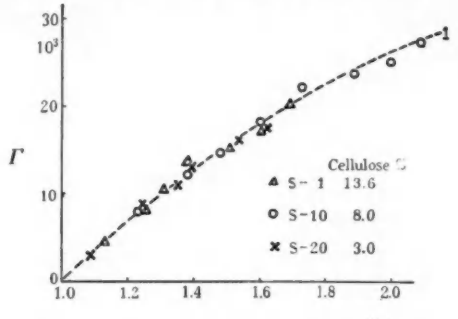


Fig. 5. Effect of the cellulose concentration

1. The effect of the concentration appears remarkably in the swelling degree of the regenerated filaments[4], but in the dry state it nearly disappears and the double refraction changes along the same course.

(4) Effect of the Drying Condition.—As is well known the drying of the freshly prepared fibre affects some properties of the fibre irreversibly and so now the effect of the air humidity in drying is observed.

For this purpose each of the two samples (S-20 and S-21) were divided into three parts and dried in the air of 30, 60 and 80% R.H. (S-20-1∼-3 and S-21-1∼-3). Each of S-21 series was further divided into two parts (S-21-1∼-3 and S-21-1′∼-3′) and the former were stored in a room controlled 70% R.H., while the latters in a desiccator of 90% R.H. They were stretched in the as me surroundings to observe the effect of the drying conditions. These air conditions are summarized in Tab. 2.

TABLE 2

Filament No.	S-20			S-21			S-21		
	1	2	3	1	2	3	1′	2′	3′
Drying: T, °C	34	34	9.5	33	18	16	33	18	16
R.H., %	30	60	80	30	60	78	30	60	78
I_{04}/I_{040}: before aging	0.656	0.678	0.692	0.666	0.675	0.687	0.666	0.675	0.687
after aging	—	—	—	0.666	0.675	0.687	0.693	0.688	0.697
Aging: T, °C					19			20	
R.H., %					70			80	
Stretching: T, °C		11–13			18–22			18–22	
R.H., %		74–79			73			87–88	

Figs. 6∼8 indicate that in the first two series the influence of different drying conditions is apparent: the filament dried at lowes R.H. has a steeper initial change while that dried at 80% R.H. shows an ordinary change. But this difference does not exist between S-21-1′∼-3′ and three curves coincide with each other and also with the curve 1.

The above phenomena may be explained by a concept that difference in drying

4) P. H. Hermans, "Physics and Chemistry of Cellulose Fibre", 1949.

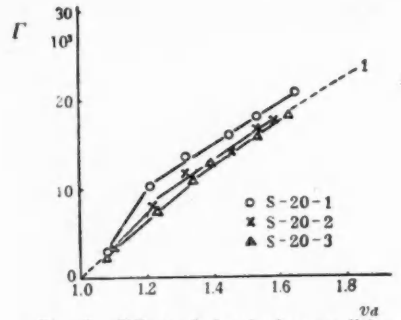


Fig. 6. Effect of the drying condition.

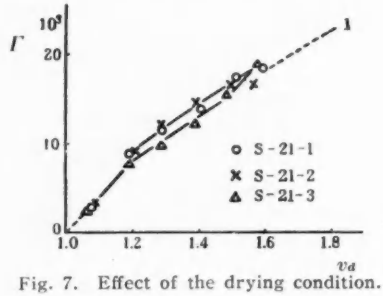


Fig. 7. Effect of the drying condition.

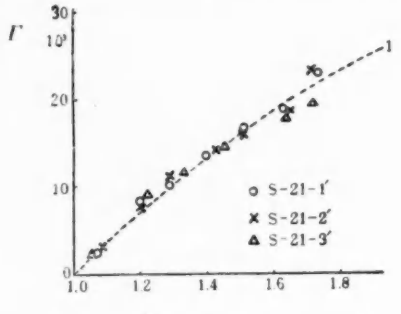


Fig. 8. Effect of the drying condition.

condition brings about some structural difference which disappears while being aged in such humid air as 90% R.H. but does not disappear in the low humidity. This concept is supported by the data in Tab. 2, according to which the dry length of the isotropic filament relative to the wet increases appreciably as the air becomes humid, and this difference disappears while the filaments are aged in 90% R.H. although it remains in the low humidity. These behaviors will have some connection with the change in weak junctions of cellulose molecules which will become less cohesive in the higher moisture content of the filament.

Summary and Discussion

Deformation of the dried filament can be expressed in the term of the first theory of Kratky on the whole as in the case of swollen filament[2]. And this behavior is not affected by the slight change of the spinning conditions of the filament such as the temperature and the composition of the cellulose solution. But in the case of the fila ment dried in the less humid air the orientation occurs more prominently in the early stage of the stretching but soon follows the above deformation mechanism.

This drying effect will illustrate the variation seen in the previous paper.[1] Of course it is noteworthy that the value of l_{0d} changes a few percent with the variation of the air humidity during measuring and, therefore, this factor must be taken into consideration when l_{0d} and l_{2d} are read under the different air conditions. Some of our older data are thought to contain small fuctuations due to this fact.

One of the authors has also reported[5] that a filament stretched in water to some degree seems to have the same molecular orientation pattern as that given by stretching in the dry state to the corresponding anisotropy and this anisotropic filament deforms further by restretching in the dry state according to the same mechanism which is shown by the isotropic filament in the dry deformation. This seemedto be a very curious and interesting fact but now becomes clear as the deformation mechanisms of the fresh (swollen) and driedfilaments are similar to each other.

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5) S. Okajima, *J. Soc. Chem. Ind. Japan*, **48**, 87, (1943); **49**, 52, (1944).

Removal of Dissolved Oxygen by Sodium Sulfite. Application to the Polarographic Study

By Shinichi KIKUCHI, Kenichi HONDA and Seckchill KIM

(Received October 20, 1953)

As is well known, in most cases of the polarographic study, the dissolved oxygen in the test solution must be removed before measuring because of its own waves which interfere with that of the substance being determined. Usually inactive gases as hydrogen or nitrogen are bubbled through the test solution for that purpose. But this is a rather time-consuming and elaborate procedure and as a result it influences the speed and efficiency of the determination. Against this physical method, the chemical method that is to adsorb the dissolved oxygen by the reducing agent, sodium sulfite, was reported by E. Varasova[1] and also was recommended by Heyrovsky[2] and Hohn[3]. Though this method seems rather simple if adequately effective, the quantitative investigation for the efficiency of sodium sulfite is not yet reported.

So there is little knowledge in the literature of the subject for the use of sodium sulfite. Of course, considering the change of the constitution of the solution which may affect the wave form of the substance being determined, its volume of addition should be as little as possible, providing it adsorbs the dissolved oxygen effectively.

From this standpoint, the effect of sodium sulfite upon the oxygen wave and its relation to the time after adding it to the test solutions were investigated. Effect to the *p*H, effect to the wave-height of the substance to be determined and effective *p*H range are also reported here.

Experimental

The concentration of dissolved oxygen was determined polarographically in the solutions of various kinds of supporting electrolyte, such as Sörensen's phosphate, glycocol-NaOH and borate-NaOH buffer solutions, 0.1M LiCl, KCl and NaOH solutions, their mixture with methanol and so on. All those solutions were made up from the reagents of "guaranteed" grade. To obtain the desired concentration of sodium sulfite, one of the freshly prepared 10, 5 and 1% solutions of it was added to the test solution. Gelatine was not used. Electrolysis was carried out in an open cell with the saturated calomel reference electrode on a liquid paraffine bath thermostatted at 25±0.1 °C. Polarographic apparatus used here was the d.c. amplification system recording polarograph which was constructed in this laboratory[4]. The capillary characteristics were 0.96 $mg^{2/3}$ $sec.^{-1/2}$ as $m^{2/3}$ $t^{1/6}$ in 0.1M KCl with no applied potential.

Results and Discussions

In order to show the concentration of dissolved oxygen, its wave-height is adopted. This is done because the object of the present study is not the direct determination of the dissolved oxygen; moreover the relative variation of dissolved oxygen corresponding to the volume of added sodium sulfite is more important. The wave-height is measured at the point of −0.5 V. vs. S.C.E. where it is accepted that there is the linear relation between the concentration and the wave-height[5].

(A) **Effect in Neutral and Alkaline Solutions.**

Concentration∼time relations are shown in Figs. 1∼7; solutions of each figure are 0.1M LiCl, KCl, phosphate buffer of *p*H 8.6, borate-NaOH buffer of *p*H 9.4.10,9,12.2 and 0.1N NaOH respectively. Each curve in the

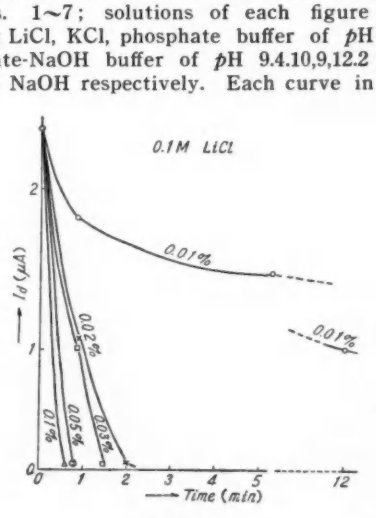

Fig. 1.

1) E. Varasova, *Collection Czech. Chem. Comms.*, **2**, 8 (1930).
2) J. Heyrovsky "Polarographisches Praktikum", Springer-Verlag, Berlin, 1948, S. 55.
3) H. Hohn, "Chemische Analysen mit dem Polarographen", Springer-Verlag, Berlin, 1937, S. 44.
4) S. Kikuchi, Y. Sakaguchi and K. Honda, This Bulletin, **25**, 98 (1952).
5) G. A. Marsh, *Anal. Chem.*, **23**, 1427 (1950).

figures represents the wave-height decrease with the time lapse after the addition of sodium sulfite; the value in percentage beside the curve shows its concentration. The wave-height at the point of time 0 indicates that of dissolved oxygen in blank solution.

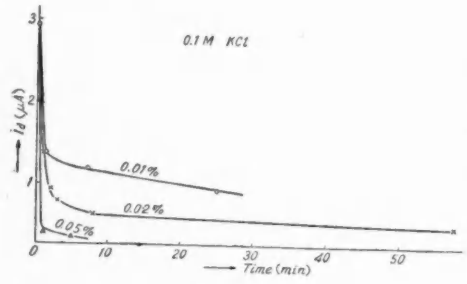

Fig. 2.

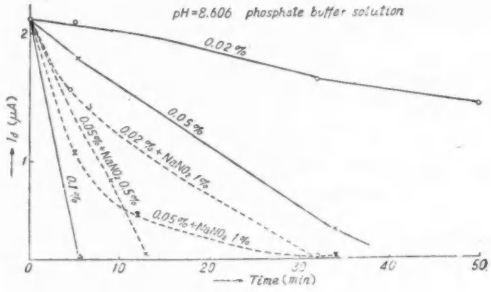

Fig. 3.

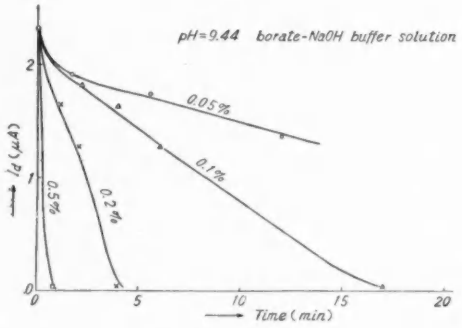

Fig. 4.

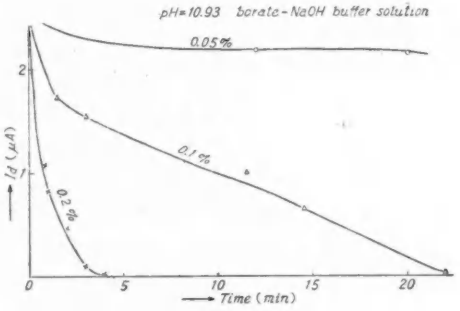

Fig. 5.

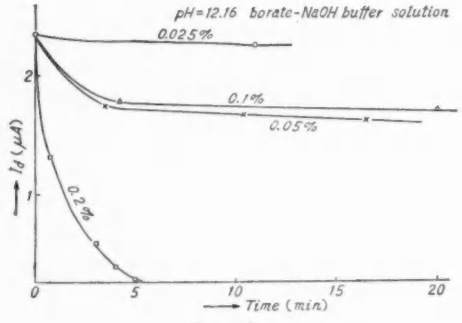

Fig. 6.

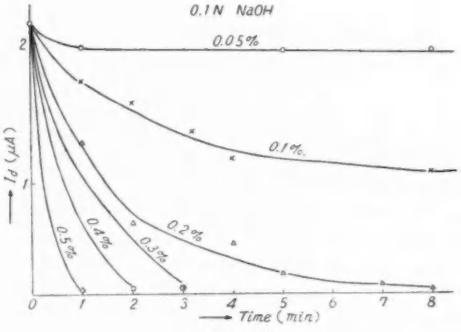

Fig. 7.

Of course, the necessary degree of removal of dissolved oxygen depends upon the magnitude of the wave to be interfered with, so minimum but adequate concentration of sodium sulfite can be determined from the figures according to the individual case. But from the practical standpoint, supposing that it is necessary that the height of the oxygen wave should decrease about one-fiftieth of ts original height within 5 minutes, the minimum concentration of sodium sulfite are as follows;

0.02%	in	0.1M LiCl
0.05	"	0.1M KCl
0.1	"	*p*H 8.6 buffer
0.2	"	*p*H 9.4 buffer
0.2	"	*p*H 10.9 buffer
0.2	"	*p*H 12.2 buffer
0.3	"	0.1N NaOH

From the figures and values above, it is

found that the reducing power of sodium sulfite is most efficient in a neutral solution and becomes less effective towards the alkaline side. The reducing reaction proceeds quickly in the first five minutes and after that proceeds more slowly.

(B) **Influence of Positive and Negative Catalyzer upon the Reducing Power of Sodium Sulfite.**

As to the reaction between oxygen and sodium sulfite, several positive and negative catalysts are described in the literature of the subject[6]. Alcohol, glycocol, aldehyde, etc. which are often encountered in organic polarography are known as negative catalyzers. In the solutions which contain the substances mentioned above, the efficiency of of sodium sulfite is markedly diminished. Those appearances are shown in Figs. 8, 9 and 10, in which the constitutions of the solutions are glycocol-NaOH buffer of *p*H 19.0, 0.1M KCl-methanol (volume ratio 1:1) and phosphate buffer of *p*H 8, 6-methanol (9:1) respectively.

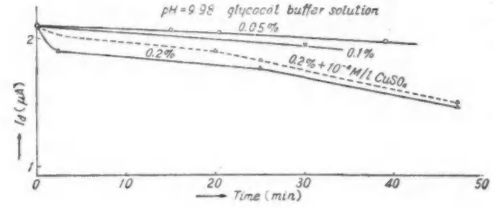

Fig. 8.

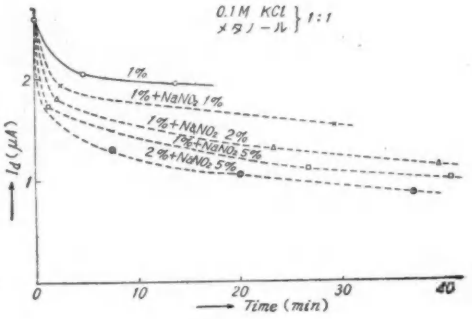

Fig. 9.

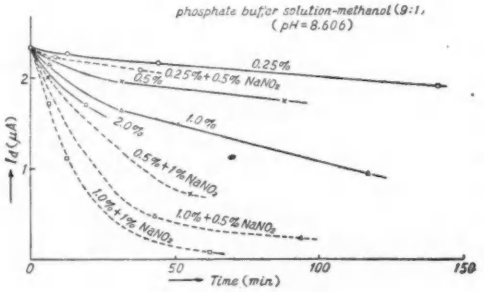

Fig. 10.

As shown in accompanying figures, the addition of sodium sulfite even up 0.2~2% is not yet sufficient and it seems unsuitable for the practical use for it may cause some important change of the constitution of the solution. To supplement this deficiency, some positive catalysts are tested. As a matter of course, it is demanded that the catalysts itself produces no reducing waves polarographically. Nevertheless, cupric sulphate is first selected, because in spite of having a well-defined wave of cupric copper, it appears at comparatively noble potential and so it seems less likely to interfere with other waves, if used in a very dilute state. Its behavior is shown as a dotted line in Fig. 8. As shown, the addition in such a concentration of 10^{-4} M/l. does not bring any effective result. But it is assumed that in the case of determination of copper the effect of sodium sulfite would be accelerated. Secondly sodium nitrite which generally is not reduced at dropping mercury electrode before the discharge of sodium ion provided that there are no polyvalent cations such as La^{+++} and Ca^{++}, is tested. Its behavior is shown as the dotted lines in Figs. 3, 9 and 10. In Fig. 3, in the phosphate buffer solution, the addition of 0.5~1% nitrite increased the removing effect somewhat more than threefold, but when the methanol content is half the volume as in Fig. 9, its effect is not so pronounced and the addition of 5% increases the power of sodium sulfite about twofold. In Fig. 10 when methanol is 10%, its catalytic effect is promoted more than before. 1% addition of nitrite promotes the reaction more than twofold.

In conclusion, when a hindering substance is contained, it is possible to remove oxygen by the addition of a promoting reagent, but from the fact of its being time-consuming, its utility still remains doubtful.

(C) **Influence to the *p*H of the Solution.**

By the addition of different substances, a change of the constitution of the solution is more or less inevitable. From the standpoint of organic polarography, the variation of *p*H value corresponding to the addition of sodium sulfite is measured roughly in the buffered solutions. The results are shown in Table 1.

6) Mellor "Inorganic and Theoretical Chemistry".

TABLE I.

Na_2SO_3	Sörensen's borate-NaOH Buffer	
%	*p*H	*p*H
0	9.29	12.12
0.05	9.3	12
0.1	9.3	"
0.5	9.5	"
1.0	9.5	"

As seen in this table, the addition causes little variation in strong alkaline solutions, but some increase of *p*H value in neutral and weak alkaline solutions and so will bring on a shift of half-wave potential of organic compounds. As a result, when the addition is more than 0.5% the calibration of *p*H is necessary even if the solution is buffered.

(D) **Influence to the Wave-height of the Substance being Determined.**

If the sodium sulfite which is known as the reducing reagent reduces the substance to be determined, its use would be nonsense. For the example of *p*-nitroanthranilic acid, this propriety is examined in the mixture of buffer solution and methanol. The wave-heights are compared in both the cases, wheh nitrogen is bubbled and when sodium sulfite in cooperation with sodium nitrite is added. The results are shown in Table II.

TABLE II. WAVE-HEIGHT OF *p*-NITROANTHRANILIC ACID

(A) 8×10^{-4} M/l. in *p*H 8.6 Buffer and Methanal (11 : 1)				
	Nitrogen passed (10 min.)		0.8% Na_2SO_3+1.2% $NaNO_2$	
Time (min.)	—	41	84	200
Wave-height (μA.)	4.2_8	4.2_8	4.2_8	4.3_9
(B) $1+10^{-3}$ M/l. in *p*H 12.2 Buffer and Methanol (9 : 1)				
	Nitrogen passed (10 min.)		0.5% Na_2SO_3+3% $NaNO_2$	
Time (min.)	—	35		77
Wave-height (μA.)	5.0_5	4.9_5		5.0_5

As shown in Table II, both wave-heights coincide within experimental error after the elapse of more than an hour. The results indicate that sodium sulfite will not affect the wave of organic compound.

(E) **Effect in the Acidic Solution.**

Hitherto it is acknowledged that the efficacy of sodium sulfite is restricted in neutral and alkaline range because on the acidic side the reduction wave of HSO^-_3 appears.[7] From the experimental result, in the buffer solution of *p*H 5.6 the oxygen wave reduces more than 90% of its original height within 10 min. Qualitatively it is found that its reducing action still proceeds in acidic solution.

As a result when the wave of the substance being determined appears at the nobler potential than that of HSO^-_3, it is possible to use this method.

7) I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, 63, 2818 (1944).

Summary

(1) From the polarographic standpoint, the behavior of reducing the dissolved oxygen by sodium sulfite is investigated in various kinds of supporting electrolytes.

(2) The efficiency is most prominent in neutral solution and becomes less effective towards basic.

(3) Influence upon the *p*H of the solution by the addition should not be neglected.

(4) There would be no effect to the reducible substance.

(5) Its reducing action still proceeds in acidic solution.

(6) The stock solution of sodium sulfite should be as fresh as possible. But a too fresh solution in 5~10 min. after preparation does not show the effect. The reason is not yet clarified. Ten or more days after preparation, it becomes less effective.

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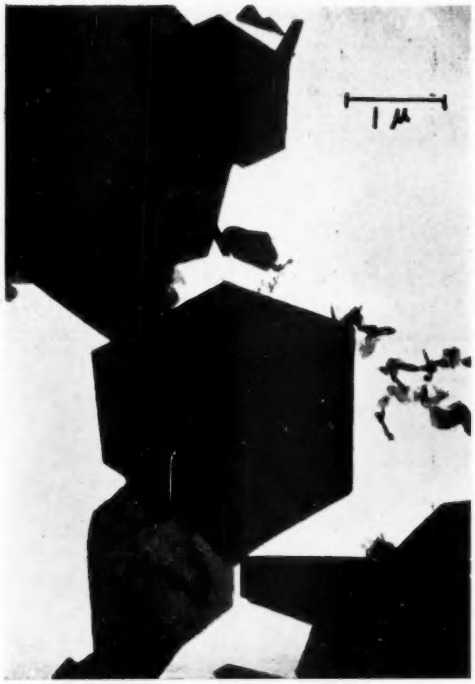


Fig. 1. Electron micrograph of the smoke of $CdCl_2$. ×15.000

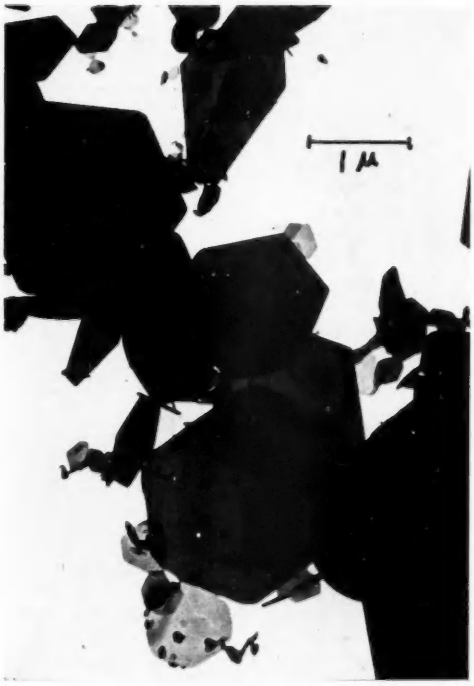


Fig. 2. Electron micrograph of the smoke of $CdBr_2$. ×15.000

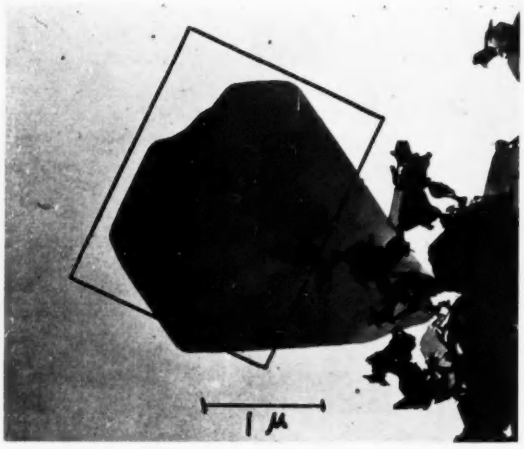
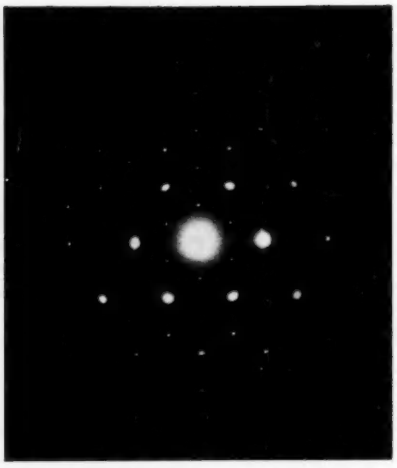


Fig. 3. (a) Electron micrograph of flakes of $CdCl_2$. ×18.000



(b) Diffraction pattern produced by transmission perpendicular to the portion indicated in the rectangle in (a).

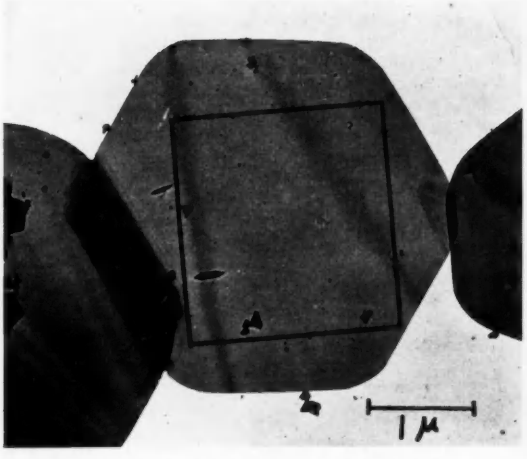
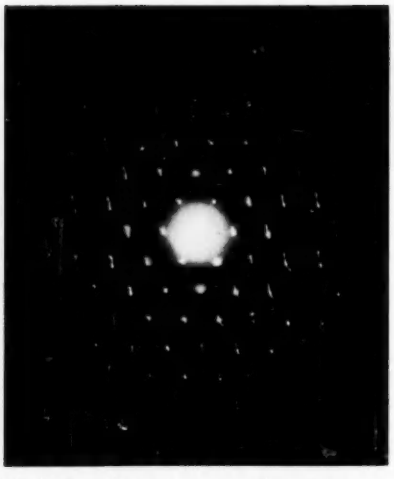


Fig. 4. (a) Electron micrograph of flakes of $CdBr_2$. ×18.000



(b) Diffraction pattern produced by transmission perpendicular to the portion indicated the rectangle in (a).

LETTER

The Study of the Smoke of $CdCl_2$ and $CdBr_2$ by Means of Electron Microscope

By Sho SUZUKI

(Received September 9, 1953)

In the course of the study of the smoke of a metal halide by means of the electron microscope[1], it was found that the smoke of $CdCl_2$ and $CdBr_2$ was made up of very thin, and hexagonal flakes. In this experiment the smoke of each cadmium halide was prepared by heating the substance in a porcelain crucible at about 800°–900°C. On heating, the substance melted at first, and then evaporated gradually in a white smoke. The smoke thus produced was deposited directly on a bronze wire screen (diameter; 0.5 mm), and was observed in the electron microscope.

Fig. 1 is the micrograph of the smoke of $CdCl_2$, and Fig. 2 that of $CdBr_2$. Both photographs reveal thin, flaky, and hexagonal crystals. The diffraction patterns of these flaky crystals were also obtained by employing the U-6 type three stage electron microscope. These flaky crystals give electron diffraction patterns as of Fig. 3(b) and 4(b). Fig. 3(b) shows the electron diffraction pattern caused by transmission nearly perpendicular to a portion of the flaky crystal of $CdCl_2$, the portion of which is indicated in the rectangle in Fig. 3(a). The electron diffraction pattern for $CdBr_2$ is shown in Fig. 4(b), and the portion of the crystal subjected to the electron diffraction is shown in the rectangle in Fig. 4(a).

The spacings for the substances are calculated from the N-pattern diagrams obtained here and are shown in Table 1, and it is confirmed that these flakes are $CdCl_2$ and $CdBr_2$. In addition, because of the hexad symmetry appearing in the N-pattern, it is evident that the electron beam is nearly perpendicular to the (III)-plane.

$CdCl_2$ and $CdBr_2$ have the typical layer structure and each layer is parallel to the (III)-plane, hence it is concluded that the flake in the present micrographs is formed as a result of the layer formation of crystals with the layer structure.

The author wishes to express his sincere appreciation to Mr. Matsuo of Shimazu Seisakusho Co. Ltd., who carried out the operation of the U-6 type three stage electron microscope, for his technical assistance, and also wishes to acknowledge the assistance of Dr. Shimazu, who gave him a chance to use the instrument.

Table I[2]

$d_{obs.}$	$d_{X\text{-ray}}$	hkl	substance
1.93	1.93	$1\bar{1}0$	$CdCl_2$
1.98	1.98	$1\bar{1}0$	$CdBr_2$

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A New Adsorption Rate Equation

By Takao KWAN

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The adsorption of nitrogen on an iron synthetic ammonia catalyst has been investigated at 300–500°C and a new adsorption rate equation

$$-\frac{dp}{dt}=k_a p\theta^{-\alpha}-k_d\theta^2 \qquad (1)$$

was found to be applicable to the experiment. Here, p the pressure of nitrogen, θ the fraction of surface covered by adsorbed nitrogen and α and k_a etc. are constants characteristic of certain intervals of surface coverage. An examination of various adsorption data so far reported indicates that this equation is of general applicability.

Eq. (1) can be expressed alternatively as,

$$\left.\begin{aligned} &-\frac{dp}{dt}=k_a p\theta^{-\alpha}\left(1-\frac{p_e}{p}\right) \\ \text{or}\quad &\log\left(-\frac{1}{p}\frac{dp}{dt}\Big/1-\frac{p_e}{p}\right)=-\alpha\log\theta+\log k_a \end{aligned}\right\} \qquad (2)$$

where p_e is the pressure of nitrogen which would be in equilibrium with θ at time t and obtainable from the data of adsorption isotherms.

If we evaluate the value of $-dp/dt$ graphically from the adsorption rate curve and plot the values of $\log\left(-\frac{1}{p}\frac{dp}{dt}\Big/1-\frac{p_e}{p}\right)$ as ordinate and $\log\theta$ as abscissa, the result is three straight lines. The inclination of the straight line is zero at a region of lower surface coverage, becoming then discontinuously steep with increasing adsorption. Such inclinations or values of α determined at 400°C are presented in the Table below.

$Fe-N_2$ $T=400°C$

θ	<0.025	$0.025<$ <0.08	$0.08<$
α	0	1.4	3.0

Adsorption isotherms were found to obey Freundlich's equation, $\log\theta=\frac{1}{n}\log P+\log K$, but the n in the equation changes discontinuously at that coverage corresponding to that of α. From the formulae of the *forward* rate and the equilibrium we can now get $k_a\theta^\beta$ for that of the reverse rate with the relation of

$$K=\left(\frac{k_a}{k_a}\right)^{\frac{1}{\alpha+\beta}},\quad n=\alpha+\beta \qquad (3)$$

If we assume that $n=1$ (Henry's law) and $\alpha=0$ in the region of low coverage and consequently $\beta=n-\alpha=1$, eq. (1) leads to its particular form

$$-\frac{dp}{dt}=k_a p-k_a\theta \qquad (4)$$

This is a Langmuir type of adsorption rate equation and was used by Barrer[1] and Kubokawa[2] respectively for $C-H_2$ and $Ni-CH_4$ with success. The adsorption rate of hydrogen on copper is proportional to hydrogen pressure in the region far removed from equilibrium[3]. This is fulfilled by eq. (4). There are also numerous other examples which follow satisfactorily eq. (2). The values of α thus determined are summarized in the accompanying Table.

System	Temp. °C	α	Ref.
$Ni-H_2$	−78	5,2	(4)
$C-H_2$	482	1,2	(5)
$ZnO-H_2$	184	3,4	(6)
$Cr_2O_3-H_2$	154	0,8	(7)
$CuCr_2O_4-O_2$	200	2,4	(8)

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The Low-temperature Luminescence Newly Found with a Number of Silver Salts

By Shoji MAKISHIMA and Takeshi TOMOTSU

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The low temperature luminescence of silver halides has been reported by several investigators[1] and been criticised recently by F. Seitz[2]. We have studied the luminescence of a number of common silver salts other than halides with a view to finding a more general relation between the luminescence and the photolytic discoloration of silver salts.

Insoluble silver salts were precipitated in the excess state of either anion or silver ion by mixing the solutions of silver nitrate and various precipitants, each of A.R. grade. At first a small quantity of precipitates was formed in the solution of both reagents by adding a small portion of the one to the other. Then the precipitates were filtered off, and finally the filtrates were mixed. The action of actinic light was carefully avoided throughout the procedures of preparation and measurements.

The luminescence was examined at room and liquid air temperature in a Dewar vessel furnished with two quartz windows under the excitation of 365 mμ of a mercury vapor lamp. The emission spectra consist of a single broad band at liquid air temperature in most cases. The luminescent characteristics are given below:

sulfite Ag_2SO_3 (orange, strong), sulfate Ag_2SO_4 (orange, medium), pyrophosphate $Ag_4P_2O_7$ (orange, medium), oxalate $Ag_2C_2O_4$ (orange, medim; white purple*, weak*), carbonate Ag_2CO_3 (red, medium), molybdate Ag_2MoO_4* (red, weak; red*, weak*), tungstate Ag_2WO_4 (red, very weak), nitrite

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$AgNO_2$* (greenish yellow, very strong; yellow*, medium*), sulfocyanide AgCNS (green, strong), cyanide AgCN (blue, medium), perchlorate $AgClO_4$ (yellow, weak), mercuri-iodide Ag_2HgI_4* (green, strong; red*, weak*).

Fluoride, nitrate, ferrocyanide, ferricyanide and phosphate are not luminescent at both room and liquid air temperatures, the last one, however, fluorescing probably infrared. The salts with asterisk are luminescent at room temperature, whose luminescence characteristics are also marked with asterisks.

Evidences were obtained that these fluorescences are not ascribed to the print-out silver. On the contrary, the fluorescences depend sometimes on whether the salt is of silver or of anion body. So, for instance, the emission color changes from silver body to anion body as follows: AgCNS (green→orange), AgCN (blue→yellowish orange), Ag_2SO_4 (orange→white purple). This indicates an intimate connection of luminescence with lattice defects. The same light as excites the luminescence leads to the blackening of the salts at higher temperature, but not at liquid air temperature. The blackening is generally less remarkable in the salts of an anion body. The authors concluded that silver salts can be luminescen in their pure state by the reverse process of photolytic absorption, in which, however, some lattice defects are undoubtedly involved. The mechanism suggested by F. Seitz, namely the transition $d^9s \rightarrow d^{10}$ within the silver ion, seems to be invalid, for similar emission spectra (orange~red) appear in some cases (as in Ag_2SO_3, Ag_2SO_4, Ag_2CO_3, $Ag_4P_2O_7$), whereas spectra are quite different with one another in other cases (as in $AgNO_2$, Ag_2HgI_4, AgCN etc.). Spectroscopic and other details are to be published in later reports.

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Additions and Corrections (supplement)

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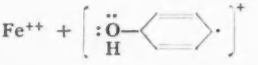
K. Inokuchi. An Improved Accurate Film Balance.

Page 474. In col. 2, line 7, for "so as not to be" read "so as to be". line 8, for "in the order to prevent" read "in order to prevent".

K. Sone. Electronic Remarks on the Origin of the Anomalous Color of Some Organic Iron. III. Complex Salts.

Page 467. In the title, for "Some Organic Iron III. Complex Salts" read "Some Organic Iron (III) Complex Salts."

Page 469. In the resonance system (1'), formulae (B) should be



H. Tsubomura. The Visible Absorption Spectra and Binding Energy of Quinhydrone-Type Molecular Compounds.

Page 304. In col. 2, line 3, for "S. Granick" read "S. Granick[4]", add to the foot-note, "(4) L. Michaelis and S. Granick, J. Am. Chem. Soc., **66**, 1023 (1944)." and shift the numbers of the remaining references in the foot-note of the paper, in the following way; (4) to (5), (5) to (6), etc.